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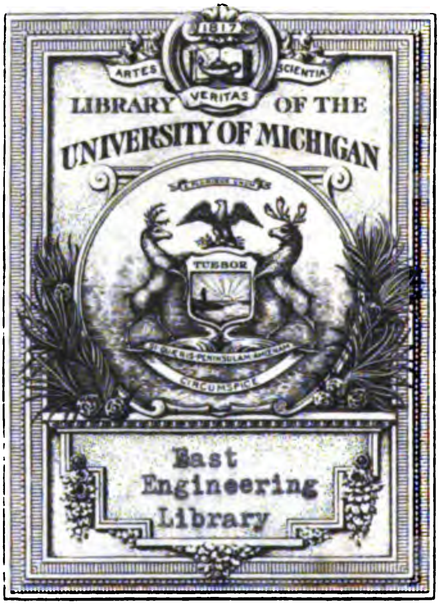

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Bulletin 1

COAL-MINING INVESTIGATIONS

UNDER AUSPICES OF

CARNEGIE INSTITUTE OF TECHNOLOGY,
UNITED STATES BUREAU OF MINES,
ADVISORY BOARD OF COAL-MINE OPERATORS
AND ENGINEERS.

THE YIELD AND QUALITY OF THE GAS, OIL, AND OTHER BY-PRODUCTS OF THE CONSTITUENTS OF THE FREEPORT COAL BED, PENNSYLVANIA.

By

JOSEPH D. DAVIS, Fuels Chemist,
United States Bureau of Mines,

and

HENRY G. BERGER, Research Fellow,
Carnegie Institute of Technology.

Price: 35 cents.

CARNEGIE INSTITUTE OF TECHNOLOGY,
PITTSBURGH, PENNSYLVANIA.
1922

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Bulletin 1

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PREFACE.

Pittsburgh is the greatest industrial center in America; and the heart of the greatest bituminous coal-mining district in the world. It is eminently desirable, therefore, that this city should have an institution which devotes a part of its great facilities to the scientific study of that branch of the industry which is largely responsible for Pittsburgh's development and that of western Pennsylvania.

On May 27, 1919, a number of the leading representatives of the coal-mining industry of western Pennsylvania met in conference with the then President of the Carnegie Institute of Technology with a view of bringing about closer relations between the Institute and the mining interests. It was felt that the advice and cooperation of men in the field were necessary for the training of young men for mining work, and at the conclusion of the meeting the following resolution was adopted:

> That this gathering give its approval and moral and material support to the form of education proposed for the Carnegie Institute of Technology by which students may receive a combined technical, practical, and business training, necessary to fit them for service in the coal mining and allied industries. Further, that the President of the Carnegie Institute of Technology appoint a board of no less than ten men representing the coal mining and allied industries, the United States Bureau of Mines, the State Department of Mines, and the Carnegie Institute of Technology, who will advise and assist in carrying out this program of education and training, particularly in its practical phases to the mining industry and in its cooperation with the United States Bureau of Mines.

Following further the intention of this resolution, the President of the Institute entered into a cooperative agreement on June 1, 1919, with the Director of the United States Bureau of Mines whereby full advantage could be taken of the Bureau's laboratories, equipment, and library, as well as of the advice and instruction of its technical staff.

To carry out this new program there was organized during the summer months the Cooperative Mining Courses in the Department of Mining and Metallurgical Engineering, College of Engineering, of the Institute. The course in mining engineering covers four years, and leads to the degree of Bachelor of Science. The two-year course in coal mining is planned to prepare men with a certain amount of practical experience for executive positions. The four-weeks intensive summer course in coal mining is designed for miners who aspire to be firebosses and mine foremen. In a large measure, the new mining, ore-dressing, and coal-washing laboratories at the Institute have been equipped gratuitously by various manufacturers of mining machinery and appliances. Cooperative research through teaching and research fellowships is devoted to various problems in coal mining and the utilization of fuels. The Institute selects the fellows; the Bureau of Mines provides the laboratory facilities; and the Advisory Board determines what problems be undertaken, and publishes the reports.

The primary object of this cooperation of the Carnegie Institute of Technology, the United States Bureau of Mines, and the Advisory Board of Coal Mine Operators and Engineers, is the proper education and training of young men for the mining industry. The ultimate objective is to bring about better conditions and greater efficiency in mining operations. The decrease in reserves of coal and increasing cost of production make it urgently necessary for mine operators and engineers to take advantage of everything which modern science, machinery, and methods can contribute.

EDWARD STEIDLE,
Supervisor, Cooperative Mining Courses,
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FOREWORD.

The investigation described in this paper was conducted by the Cooperative Mining Courses of the Carnegie Institute of Technology and the Pittsburgh Experiment Station of the U. S. Bureau of Mines in cooperation with the coal-mining industry of western Pennsylvania. Under cooperative agreement four research fellowships paying $750 per annum per year of 10 months are supported by the Carnegie Institute of Technology. These fellowships are open to properly qualified graduates of universities and technical schools. The research work is carried on in laboratories of the Bureau of Mines under the direction of a member of the Bureau's research staff, and is published under the joint authorship of the two investigators.

Fellowship holders are required to register at the Institute as graduate students, and become candidates for the degree of Master of Science, unless an equivalent degree has been previously earned. The purpose of these fellowships is the solution of problems in mining and utilization of coal.

The study of the gas, oil, and other by-products of the constituents of the Freeport coal bed was undertaken at the suggestion of the Advisory Board of coal operators, with a view to obtaining experimental data on the possibility of utilizing the cannel and bone constituents of the Freeport coal bed with the recovery of oils and other by-products in a similar manner as proposed for oil shales. The tests showed that the cannel coal yields from 27 to 33 gallons of tar oils, 3800 to 4500 cubic feet of gas, 9 to 10 pounds of ammonium sulphate, and 75 per cent of rather high-ash smokeless fuel per ton of raw material carbonized at low temperatures. It is probable that in the relatively near future this cannel coal, which is now wasted, can be economically carbonized at low temperatures; but it is doubtful whether bone coal can be so treated. The time when such low-temperature carbonization can be economically undertaken depends on the rate of diminution of petroleum resources. The report also contains data on results of low-temperature carbonization of the various benches of good coal in the Freeport bed.

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The writers wish to express their appreciation for the many helpful suggestions of A. C. Fieldner, superintendent and supervising chemist of the Pittsburgh Experiment Station of the Bureau of Mines, and J. J. Jakowsky, assistant petroleum chemist. Valuable assistance in the correlation of microstructure with by-product yields was rendered by Reinhardt Thiessen, microscopist, and A. W. Voorhees, then research fellow of the Carnegie Institute of Technology.

The writers also wish to take this opportunity to acknowledge the excellent cooperation and willing help given by Edward Steidle, supervisor, Cooperative Mining Courses, and the officials of the mines from which coal samples were procured; especial assistance being rendered by A. R. Pollock, general manager, Ford Collieries Co., and H. J. Nelms, superintendent, New Field By-Product Coal & Coke Co.

THE YIELD AND QUALITY OF THE GAS, OIL, AND OTHER BY-PRODUCTS OF THE CONSTITUENTS OF THE FREEPORT COAL BED, PENNSYLVANIA.

By JOSEPH D. DAVIS and HENRY G. BERGER.

INTRODUCTION

Anticipated shortage of hydrocarbon oils in the future, owing partly to increased demand by the automotive industry and partly to failure of natural resources, has led investigators to consider materials other than petroleum as a source of supply. An enormous amount of experimental work has been done on the recovery of such oils, both from oil-shales and from coals by destructive distillation. The distillation methods used are generally characterized as low-temperature methods to distinguish them from the commercial high-temperature retorting method where gas and metallurgical coke are the main products sought. The chief advantage of low-temperature distillation is that a much greater yield of tar oils is obtained. Further, the oils are of better quality—that is, they contain a lower percentage of thermal decomposition products such as olefines and aromatic complexes, which are difficult to refine by methods at present known.

It is not the purpose of the writers to discuss at length the relative merits of coal and oil-shale as raw materials, but it would seem that coal has the advantage in one respect at least, namely, the residue from coal has a high fuel value, and, in general, is marketable without further treatment; whereas the oil-shale residue is of doubtful value.

Distillation residues from those portions of a coal seam looked upon as mine waste should have some fuel value, and such oils and other products as might be obtainable from waste, it was argued, would be equal in quality to those from the true coal. In order to check this point, it was decided to subject samples from all partings of a coal seam to the same distillation process, and then compare the products. An additional incentive to this work was the opportunity for correlating the results of distillation with those of a microscopic examination of the same seam being carried on at the same time by Reinhardt Thiessen and A. W. Voorhees, results of which are being published as a companion paper (Bull. 2) to this one.

PURPOSE OF INVESTIGATION

The purpose of this investigation was (1) to study the low-temperature carbonization products yielded by the waste coals of the Upper Freeport seam with a view to their possible utilization; (2) to compare these products with those from the true coals; and (3) to determine if the distillation products would show any consistent variation in character with varying microstructure of the coal.

HISTORY AND SCOPE OF PREVIOUS INVESTIGATIONS.

Until about 1880, nearly all coal was carbonized in beehive ovens which produced excellent metallurgical coke, but with a complete loss of the by-products. However, as early as 1850, attempts were made in the recovery of by-products, and by 1873, by-product coke ovens began to be used extensively. By 1885, great progress had been made in the development of by-product ovens, and shortly after that time their use became almost universal in Europe. The United States, however, was slow in adopting the new form of oven, and in 1900, only about 5 per cent of the coke output was produced thereby. At the present time, by-product coking is standard practice, and in 1921, the output therefrom was 78 per cent of the total of 25,400,000 tons of coke made by the two methods.

In recent years, by-product coking at low temperatures has received much attention, and fuel technologists in America, England, and Europe, have been and are still experimenting with such processes, the main purpose being the utilization of special products yielded by low-temperature treatment. It has been found that at 600° C., from 85 to 90 per cent of the volatile matter of coal is distilled off, removing those heavier hydrocarbons which are responsible for the production of smoke in ordinary combustion. The residue from such distillation is an easily ignitable solid of varying physical properties, which should be well adapted for use as smokeless fuel. The tars produced in this low-temperature work differ greatly from those produced by the usual high-temperature operation. They are more fluid than the tars of present by-product distillations, and have a higher content of recoverable oils and a very low free-carbon content. The gases produced are of high-heating value, although considerably less in quantity than the gases from the high-temperature distillations.

In his work on Illinois coals, Parr[1] found that they could be coked at 400 to 450° C., yielding a gas of high candle-power. About 20 per cent of the nitrogen was recovered as ammonia. The condensable distillate consisted mainly of oils with little free carbon and of low pitch content. He considered the coke especially valuable as a concentrated, smokeless fuel.

---

[1] Parr, S. W., University of Illinois Eng. Sta. Bull. 60, 1912, p. 26.

In another more recent paper, Parr[2] defined low-temperature carbonization as destructive distillation at temperatures not to exceed 750 to 800° C. A coal which would yield only 10 gallons of condensable distillates per ton with high temperatures would give from 20 to 25 gallons per ton with the above-mentioned temperature limits. He found the decomposition procedure to be as follows:

1. From 250 to 300° C., water was given off.
2. From 300 to 350° C., CO_2 appeared in quantity.
3. From 350 to 400° C., CH_4 was liberated rapidly.
4. At the last stage, ethane and heavier gases began to appear, and also the tar acids.

There was an absence of secondary reactions, resulting in a thin, light tar, free from naphthalene. The gas yield was from 60 to 80 per cent of that from high-temperature processes.

Using 500° C. as his maximum temperature, Lewes[3] obtained results agreeing with those of Parr. He reported low percentages of benzene, but large quantities of paraffins, such as hexane, heptane, and octane; also considerable quantities of naphthenes. Carbolic acid was present in the oils only in small quantities, while its higher homologues, such as cresylic acid, were present in larger quantities. The free carbon content was less than 2 per cent.

The work of L. T. Wright[4], done at 600° C. to ordinary retort temperatures, showed distinctly the change in composition of coal tars with increase in distillation temperatures, although he did not give the exact temperatures at which the distillations were made.

Burgess and Wheeler[5], in the distillation of 200-gram samples of bituminous coal at temperatures ranging from 100 to 450° C. for 4 to 8 weeks at a vacuum of 20 mm., obtained data from which they drew the following conclusions:

1. Occluded or "condensed" gases and higher paraffin hydrocarbons are involved up to 150° C., or even 200° C.

2. At 200° C. there is a copious evolution of water, which continues up to and probably a little beyond 450 degrees.

3. Between 270 and 300° C., hydrogen sulphide (H_2S) is evolved, most likely from the decomposition of organic sulphur

---

[2] Jour. Ind. & Eng. Chem., vol. 13, No. 1, 1921, p. 14.

[3] Lewes, V. B., The carbonization of coal, 1912, vol. 1, p. 192.

[4] Loc. cit.

[5] Burgess, M. J., and Wheeler, R. B., Jour. Chem. Soc., vol. 97, 1910, p. 1917; vol. 99, 1911, p. 649; vol. 105, 1914, p. 131.

compounds. At this temperature also, olefines higher than ethylene appear. They fall off or disappear at 350° C.

4. A reddish-brown oil distills over at 310° C., and is not considered a decomposition product.

5. The critical point of decomposition occurs at 350° C., as is shown by a marked increase of gas production and the appearance of a viscous oil.

6. The gaseous hydrocarbons evolved up to 450° C., consist of methane, ethane, propane, butane, and also pentane, as well as ethylene and higher unsaturated hydrocarbons.

7. Neither benzene nor its homologues could be detected as condensable, and their formation at such low temperatures is doubted.

These results led Burgess and Wheeler to investigate the yields from four representative British coals at constant temperatures between 450 and 1000° C., and from their results they concluded that coal contains two distinct types of organic compounds, one decomposing readily, yielding paraffin hydrocarbons and no hydrogen; the other decomposing less readily and yielding hydrogen alone, or with oxides of carbon. The experimental facts observed above have been verified by Vignon[6], but his opinions differed in regard to the interpretation of the results.

H. C. Porter and G. B. Taylor[7] disagreed decidedly with the view that the rapid increase in evolution of hydrogen would indicate a critical period after which the paraffin yielding resinic compound is completely decomposed, and the hydrogen-yielding cellulosic compound begins to decompose. They declared that the sudden evolution of hydrogen is due to a secondary decomposition reaction of the tars. Furthermore, Jones[8], in a study of the thermal decompositions of low temperature tars, found a rapid increase in hydrogen production between 750 and 800° C. One of the conclusions he draws from this observation is that high-temperature tars are formed by the decomposition of low-temperature tars, definitely arguing against the "two compound" theory of Burgess and Wheeler.

TYPES OF COAL USED.

The coal used in these experiments were bituminous, cannel and bone coals which separate the benches of the true coals, taken from three mines in the Freeport seam, a typical cross-section of which is shown in the table below. The Freeport seam is in the carboniferous system, Pennsylvania series, and at the top of the Allegheny formation. The following mines were sampled: Frances, Ford Collieries Company, Curtisville, Pa.; New Field, New Field By-Product Coal & Coke Co., Piercedale, Pa., and the Creighton, Pittsburgh Plate Glass Company, Creighton, Pa.

---

[6] Vignon, Leo, Fractional distillation of coal, Compt. Rend., vol. 155, 1912, p. 1514.

[7] Proc. Am. Gas Inst., vol. 9, 1914, p. 234.

[8] Jones, D. T., The thermal decomposition of low-temperature coal tar, Jour. Soc. Chem. Ind., vol. 36, 1917, pp. 3-7.

Typical section of Freeport coal bed.

	Inches.
Cannel coal	⅛ to 33
Coal	34
Bone coal	8 to 12
Coal	33
Shale	1
Coal	3
Shale	1
Coal	6
Clay	—

The 9 inches of coal below the first layer of shale is seldom mined; the bone coal is refuse which goes to the dump, while the cannel coal is left in the mines, making a good roof.

The cannel coals from the Freeport seam are different from the typical cannel coals in that they might be said to be half-way between a coal and a cannel coal, and in this respect approach a bituminous shale. Their ash content (26 to nearly 29 per cent, see table 1) is high, but varies through the seam; while the volatile matter is somewhat less than that of the coal from this seam. The sulphur content tends to be less than that of the coals. The bone coals have an exceedingly high ash content, and from 10 to 12 per cent less volatile matter than the coal. The Freeport coal analyzed varied in ash content from 6.65 to 9.88 per cent, while the volatile matter averaged about 37 per cent. There was a wide variation in the sulphur content.

DETAILS OF EXPERIMENTS.

Apparatus.—The apparatus used is shown in figure 1 and plate 1. The coal was distilled in an electrically heated retort *e*, 6 inches in diameter. A shelf was placed in the retort held up by sleeve *d* to protect the coal body from the cold end. At *c* is a transformer for temperature control, and *b* is an ammeter. A chromel-alumel thermocouple *a* was introduced into the center of the mass, allowing temperature readings from bottom to top. A Leeds and Northrup potentiometer was used for temperature measurements.

The distillates were partly condensed in an air condenser *g* from which they were conducted to a water condenser *h*, where all the condensates were collected. From there the gases were passed through an adaptation of the Cottrell electric precipitator

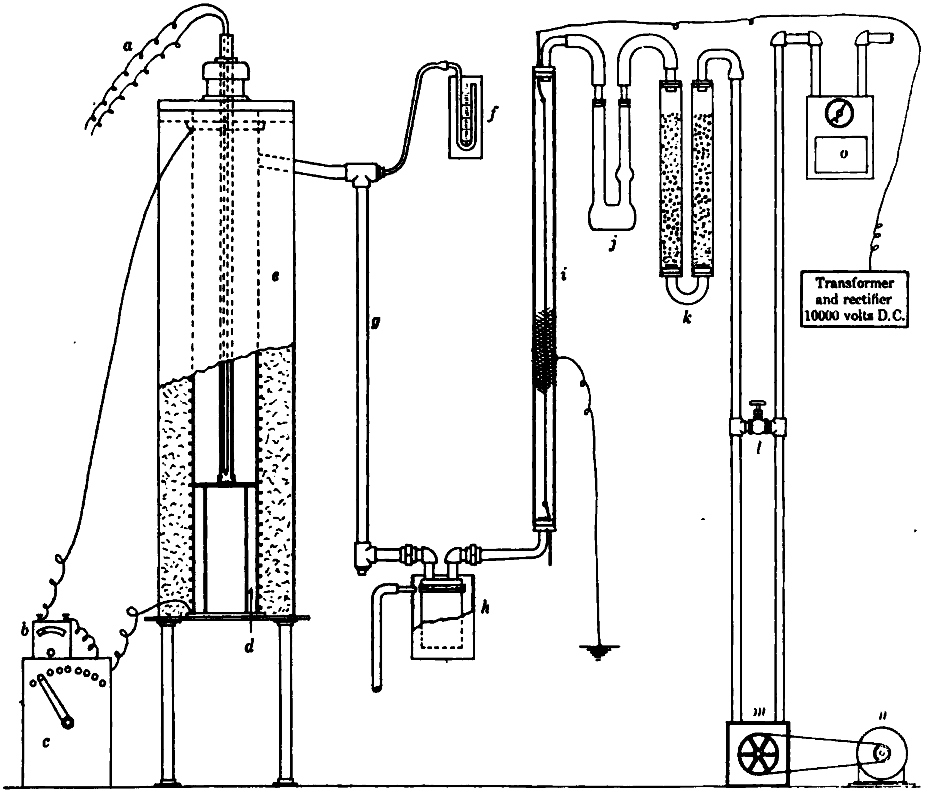

FIGURE 1.—*Diagram of apparatus for the low-temperature carbonization of coals.*

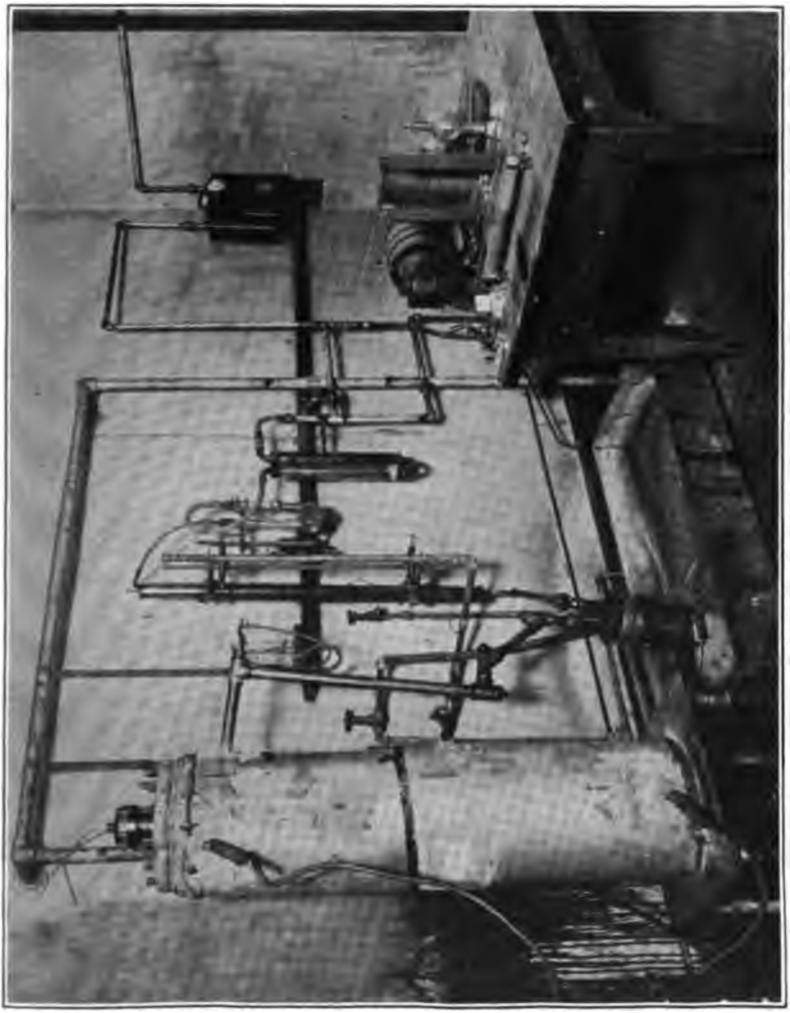

Plate I.—*View of apparatus as set up.*

TABLE 1.—*Coal analyses.*

	Proximate analysis.				Ultimate analysis.					Calorific value B. t. u.
	Moisture.	Volatile matter.	Fixed carbon.	Ash.	Hydrogen.	Carbon.	Nitrogen.	Oxygen.	Sulphur.	
Cannel coal, Frances mine (air dry loss 0.6)	(1) 1.46	30.34	42.08	26.12	4.20	60.84	1.25	6.72	0.87	10942
	(2) 0.88	30.52	42.32	26.28	4.15	61.20	1.25	6.24	0.88	11007
	(3)	30.79	42.70	26.51	4.10	61.74	1.27	5.50	0.88	11104
	(4)	41.90	58.10	.....	5.58	84.01	1.73	7.48	1.20	15110
Cannel coal, roof of Creighton mine (air dry loss 0.2)	(1) 0.49	30.71	40.13	28.67	4.45	60.44	1.19	4.48	0.77	10979
	(2) 0.28	30.77	40.22	28.73	4.44	60.57	1.19	4.30	0.77	11002
	(3)	30.86	40.33	28.81	4.42	60.74	1.20	4.06	0.77	11033
	(4)	43.35	56.65	.....	6.21	85.32	1.69	5.70	1.08	15498
Upper bench, Freeport coal (air dry loss 1.10)	(1) 2.14	37.19	54.06	6.61	5.32	77.00	1.60	7.78	1.69	13875
	(2) 1.05	37.60	54.67	6.68	5.26	77.86	1.62	6.87	1.71	14029
	(3)	38.00	55.25	6.75	5.19	78.68	1.63	6.02	1.73	14178
	(4)	40.75	59.25	.....	5.57	84.38	1.75	6.44	1.86	15204
Upper bench, Freeport coal, New Field mine (air dry loss 0.4)	(1) 4.21	37.03	49.62	9.14	5.85	69.30	1.48	12.35	2.38	12472
	(2) 3.83	37.17	49.82	9.18	5.83	69.57	1.49	12.04	2.39	12521
	(3)	38.66	51.80	9.54	5.09	72.35	1.55	8.99	2.48	13020
	(4)	42.74	57.26	.....	5.63	79.98	1.71	9.94	2.74	14393
Bone coal, Frances mine (air dry loss 1.1)	(1) 2.43	24.54	36.87	36.16	3.86	50.76	1.05	7.63	0.54	8897
	(2) 1.38	24.80	37.27	36.55	3.78	51.30	1.06	6.76	0.55	8992
	(3)	25.15	37.79	37.06	3.68	52.02	1.08	5.61	0.55	9119
	(4)	39.96	60.04	.....	5.85	82.65	1.72	8.91	0.87	14488
Bone coal, New Field mine (air dry loss 0.0)	(1) 0.70	25.40	36.62	37.28	3.66	50.91	1.00	6.17	0.98	9064
	(2) 0.70	25.40	36.62	37.28	3.66	50.91	1.00	6.17	0.98	9064
	(3)	25.58	36.88	37.54	3.59	51.27	1.01	5.60	0.99	9128
	(4)	40.95	59.05	.....	5.75	82.08	1.62	8.96	1.59	14614
Lower bench, Freeport coal, Frances mine (air dry loss 1.0)	(1) 2.64	34.87	55.91	6.58	5.40	78.14	1.68	7.46	0.74	13870
	(2) 1.65	35.23	56.47	6.65	5.34	78.94	1.70	6.62	0.75	14010
	(3)	35.82	57.42	6.76	5.25	80.26	1.73	5.24	0.76	14246
	(4)	38.42	61.58	.....	5.63	86.00	1.86	5.61	0.82	15279
Lower bench, Freeport coal, New Field mine (air dry loss 0.5)	(1) 4.07	36.47	49.63	9.83	3.18	68.29	1.49	12.20	3.01	12300
	(2) 3.60	36.65	49.87	9.88	5.16	68.63	1.50	11.81	3.02	12361
	(3)	38.02	51.73	10.25	4.93	71.19	1.55	8.94	3.14	12822
	(4)	42.36	57.64	.....	5.49	79.32	1.73	9.96	3.50	14286
Creighton mine, below floor, just above fireclay (air dry loss 0.7)	(1) 0.99	38.59	51.98	8.44	5.17	74.11	1.49	6.41	4.38	13600
	(2) 0.28	38.87	52.35	8.50	5.13	74.64	1.50	5.82	4.41	13697
	(3)	38.98	52.58	8.52	5.11	74.85	1.50	5.60	4.42	13736
	(4)	42.61	57.39	.....	5.59	81.82	1.64	6.12	4.83	15015

(1)—as received. *(2)—air dried.* *(3)—moisture free.* *(4)—moisture and ash free.*

i, which removed the final traces of tar mists from the gases. In *j* is an ammonia scrubber, and *k* is a U-tube of activated charcoal for the removal of light oils from the gas, which was measured by meter *o*. The system was kept at atmospheric pressure by a Crowell pump *m*, the gases being collected over water in gas tanks from which the samples for analysis were taken.

Method of distillation.—Coal weighing 5675 grams (12.5 lb.) ranging in size up to ½ inch, was used in every charge. The charge was put into the cold retort and gradually heated to a temperature of about 600° C., and kept at that point until the decrease in rate of gas evolution indicated an equilibrium at that temperature. The rate of heat input was kept constant, and the time required for a complete distillation varied from 6 to 8 hours.

The clean coals showed a strong exothermic reaction beginning at 550 to 600° C. This phenomenon was also observed by Hollings and Cobb[9]. The total liquid condensates were caught in one container and weighed. The gases were measured by a meter and stored in a tank over water. After a distillation, a sample of the total gas was taken for analysis.

DISCUSSION OF RESULTS.

Table 2 is a survey of yields of gas, tar, and coke obtained in these experiments.

TABLE 2.—*Survey of yields.*

Coal.	Coke, per cent.	Tar and water, per cent.	Dry tar per ton, gallons.	Gas per ton, cu. ft.	Remarks.
Cannel coal, Frances mine....	74.7	16.0	27.5	3810	Non-fused residue; original pieces intact. Plate II. Tar approximately 31% H_2O by weight.
Cannel coal, Creighton mine.........	74.5	17.8	33.5	4540	Non-fused residue; original lumps intact. Plate III. Tar 30% H_2O.
Upper bench, Freeport coal, Frances mine....	68.6	19.7	26.0	7175	Fairly good coke. Plate IV. Tar 23% H_2O.
Upper bench, Freeport coal, New Field mine....	67.5	19.6	28.0	7450	Fair coke. Plate V. Tar 23% H_2O.
Bone coal, Frances mine....	78.2	13.1	13.0	3635	Partly fused coke, very friable with some unchanged lumps mixed throughout. Plate VI. Tar 51.5% H_2O.
Bone coal, New Field mine....	79.5	12.5	14.0	3460	Partly fused coke—friable. Some unchanged lumps throughout. Plate VII. Tar 42% H_2O.
Lower bench, Freeport coal, Frances mine....	69.5	19.1	23.5	8360	Fairly good coke. Plate VIII. Tar 36% H_2O.
Lower bench, Freeport coal, New Field mine....	68.8	17.8	25.0	8160	Fair coke. Plate IX. Tar 25% H_2O.
Coal below floor just above fireclay, Creighton mine...	67.0	19.7	27.5	8225	Fair coke. Plate X. Extremely high in sulphur. Tar 26% H_2O.

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[9] Hollings, Harold, and Cobb, J. W., A thermal study of the carbonization process, Jour. Chem. Soc., vol. 107, 1915, pp. 1106-1115.

Gas.—The yield of gas was low when compared with high-temperature results. The clean coal gave an average of 3.9 cubic feet per pound of coal, and the cannel coal an average of 2 cubic feet, while the bone coal yielded only 1.75 cubic feet. There was practically no difference in heating value between the gas from the bone coal and that from the regular Freeport coal. The cannel coal, however, produced a somewhat richer gas. On the basis of total B. t. u. per ton of coal, even the bone coal would deliver enough gas for heating the ovens and carrying out the process. Analyses of the gases are shown in table 3. Attention is drawn to the similarity of the gases from the bone and regular Freeport coals. The cannel coal gas contains about 33 per cent as much hydrogen as the other gases, and greater quantities of methane and ethane.

Coke.—This is probably the most important product of any low-temperature process. The yields of coke from the regular Freeport coals averaged about 68 per cent of the coal used, the lower seam producing slightly higher yields than the upper seam. (See table 4 for analyses.) The coke appeared to be of a good texture and fairly dense in structure. (See plates II to X, inclusive. The numbers on the samples refer to distillation runs only.) According to all indications, the cokes would be well suited for domestic use, but probably not for metallurgical purposes, judging from present specifications. The ash content of the cokes varied from 7.5 to 12 per cent, comparing favorably with anthracite coal. The volatile matter content ranged from 1.5 to 4.5 per cent. Judging by the work of other investigators, it was expected that the coke would contain more volatile matter—perhaps 8 or 10 per cent; and that it would be similar in that respect to British low-temperature semi-coke. It was therefore thought possible that some parts of the coke actually might have been subjected to a higher temperature than the 600° C. fixed upon. To check this point, coking tests were made in a small tube furnace wherein temperature and control of heating rate could be made certain. Analyses of the test coke showed that the volatile content was not over 5 per cent in any case. This proved that the cokes obtained in the larger scale work contained about the amount of volatile matter to be expected. It may be taken as proved, then, that a maximum temperature of 600° C. is too high when it is desired to make semi-coke from Freeport coal, and 600° C. is possibly too low for the production of metallurgical coke from this coal; but it would seem practical to make such coke by raising the temperature only slightly, say to 750° C., without sacrificing much

TABLE 3.—*Gas analyses.*

Gas.	Cannel coal, Frances mine.	Cannel coal, Creighton mine.	Upper bench, Freeport coal, Frances mine.		Upper bench, Freeport coal, New Field mine.	Bone coal, Frances mine.		Bone coal, Frances mine*.	Bone coal, New Field mine.	Lower bench, Freeport coal, Frances mine.	Lower bench, Freeport coal, New Field mine.		Coal below floor, Creighton mine.
CO_2	5.1	2.4	2.4	2.7	2.33	2.1	1.75	1.9	2.42	2.36	2.9	2.06	3.4
C_2H_4, etc.	3.3	2.26	3.3	3.9	3.33	1.5	3.15	1.0	2.18	3.64	2.4	2.97	2.9
O_2	0.0	0.0	0.4	0.3	0.0	0.0	0.00	0.0	0.00	0.00	0.0	0.00	0.5
H_2	17.4	17.4	46.2	47.2	48.4	43.0	46.3	59.8	39.4	51.4	40.0	50.6	50.0
CO	8.6	5.0	4.8	5.5	4.67	6.2	5.6	7.25	4.7	5.25	4.5	4.57	4.6
CH_4	53.5	50.4	35.0	33.7	32.6	37.3	36.0	24.10	39.0	32.30	41.2	35.6	32.7
C_2H_6	12.1	10.9	4.7	4.4	4.67	5.2	2.5	1.9	5.4	5.05	6.3	4.2	4.1
N_2	0.0	12.2	3.2	2.3	4.0	3.9	4.7	3.8	6.9	0.0	2.7	0.0	1.8
B. t. u. per cu. ft. (calculated)	915.6	826.7	679.3	681.2	661.6	663.6	646.6	518.1	679.8	684.2	727.7	685.5	648.3

**Gas obtained from heating No. 6 up to 900° C. after by-products had been removed and charge cooled.*

PLATE II.—*Residue from cannel coal, Frances mine.*

PLATE III.—*Residue from cannel coal, Creighton mine.*

PLATE IV.—*Coke from upper bench Freeport coal, Frances mine.*

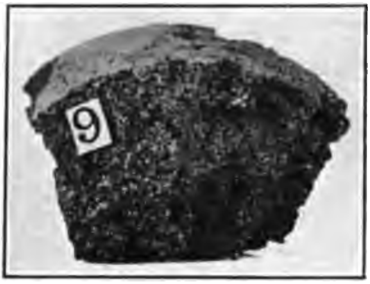

PLATE V.—*Coke from upper bench Freeport coal, New Field mine.*

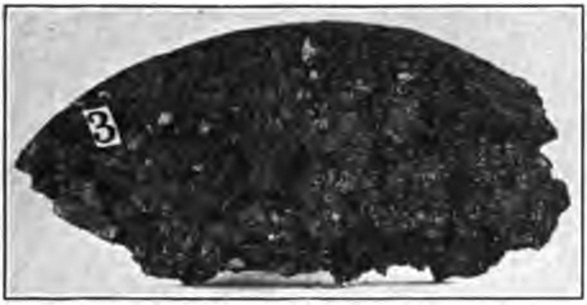

PLATE VI.—*Residue from bone coal, Frances mine.*

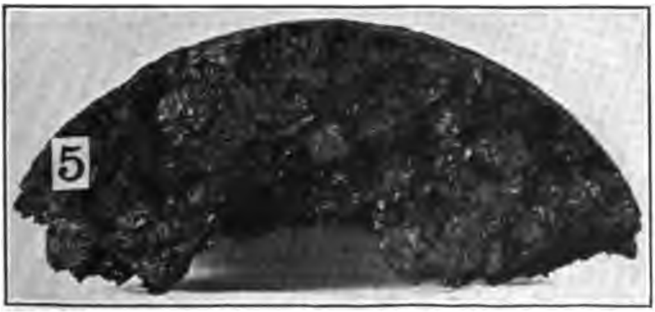

PLATE VII.—*Residue from bone coal, New Field mine.*

Plate VIII.—*Coke from lower bench Freeport coal, Frances mine.*

Plate IX.—*Coke from lower bench Freeport coal, New Field mine.*

Plate X.—*Coke from coal below floor just above fireclay, Creighton mine.*

of the tar. The gas yield would, of course, be improved by such a procedure.

Extensive use of such low-temperature cokes for domestic purposes would solve completely the problem of smoke abatement, so important in many large cities. Economically, it would be a big factor in the conservation and complete utilization of our fuel resources.

The cannel coal residue was unchanged in form from the original cannel coal. There had been no fusion in the carbonization process, merely a few cleavages in the lumps to allow passage of the vapors. The remaining volatile matter varied from 1.5 to 3 per cent, while the ash content was as high as 35 per cent.

TABLE 4.—*Coke analyses.*

Coals from which the cokes have been derived.		Proximate analysis.				Ultimate analysis.					Calorific value, B. t. u.
		Moisture.	Volatile matter.	Fixed carbon.	Ash.	Hydrogen.	Carbon.	Nitrogen.	Oxygen.	Sulphur.	
Cannel coal, Frances mine	1*	0.70	1.45	61.52	36.33	0.59	60.45	0.62	1.38	0.63	9234
	2.	....	1.46	61.95	36.54	0.51	60.88	0.62	0.77	0.63	9299
	3.	....	2.30	97.70	.....	0.80	96.01	0.98	1.22	0.99	14665
Cannel coal, Frances mine	1.	1.73	3.00	61.54	33.73	1.62	60.20	1.13	2.78	0.54	9575
	2.	....	3.05	62.63	34.32	1.46	61.26	1.15	1.26	0.55	9744
	3.	....	4.64	95.36	.....	2.22	93.27	1.75	1.92	0.84	14836
Cannel coal, Creighton mine	1.	0.48	3.40	61.22	34.90	1.50	60.23	1.17	1.67	0.53	9486
	2.	....	3.42	61.51	35.07	1.46	60.52	1.18	1.24	0.53	9532
	3.	....	5.27	94.73	.....	2.25	93.21	1.82	1.90	0.82	14680
Upper bench, Freeport coal, Frances mine	1.	1.70	2.78	85.49	10.03	1.63	83.54	1.57	1.76	1.47	13080
	2.	....	2.83	86.97	10.20	1.46	84.98	1.60	0.26	1.50	13306
	3.	....	3.15	96.85	.....	1.63	94.63	1.78	0.29	1.67	14817
Upper bench, Freeport coal, Frances mine	1.	0.18	1.50	87.97	10.35	1.10	85.15	1.60	0.33	1.47	13144
	2.	....	1.50	88.13	10.37	1.10	85.30	1.60	0.16	1.47	13168
	3.	....	1.67	98.33	.....	1.23	95.17	1.79	0.17	1.64	14692
Upper bench, Freeport coal New Field mine	1.	1.78	2.67	83.42	12.13	1.57	80.75	1.54	2.09	1.92	12610
	2.	....	2.72	84.93	12.35	1.39	82.21	1.57	0.53	1.95	12838
	3.	....	3.10	96.90	.....	1.59	93.79	1.79	0.61	2.22	14647
Bone coal, Frances mine	1.	0.20	0.48	48.29	51.03	0.52	46.26	0.50	1.28	0.40	7061
	2.	....	0.48	48.39	51.13	0.50	46.36	0.50	1.11	0.40	7075
	3.	....	0.98	99.03	.....	1.02	94.86	1.02	2.28	0.82	14477
Bone coal, Frances mine	1.	0.23	3.47	48.35	47.95	1.33	47.79	0.91	1.31	0.71	7698
	2.	....	3.48	48.46	48.06	1.31	47.90	0.91	1.11	0.71	7716
	3.	....	6.70	93.30	.....	2.52	92.22	1.75	2.14	1.37	14856
Bone coal, New Field mine	1.	0.35	3.08	46.44	50.13	1.29	45.64	0.88	1.66	0.40	7284
	2.	....	3.09	46.60	50.31	1.25	45.80	0.88	1.36	0.40	7310
	3.	....	6.22	93.78	.....	2.52	92.17	1.77	2.74	0.80	14711
Bone coal, New Field mine	1.	1.38	3.87	50.17	44.58	1.33	50.36	0.93	2.11	0.69	7936
	2.	....	3.92	50.88	45.20	1.20	51.06	0.94	0.90	0.70	8047
	3.	....	7.15	92.85	.....	2.19	93.18	1.72	1.63	1.28	14684
Lower bench, Freeport coal, Frances mine	1.	0.08	1.57	88.12	10.23	1.32	85.44	1.59	0.98	0.44	13132
	2.	....	1.57	88.19	10.24	1.31	85.51	1.59	0.91	0.44	13143
	3.	....	1.75	98.25	.....	1.46	95.26	1.77	1.02	0.49	14642
Lower bench, Freeport coal, New Field mine	1.	2.05	4.33	85.94	7.68	1.94	84.10	1.56	3.80	0.92	13296
	2.	....	4.42	87.74	7.84	1.75	85.86	1.59	2.02	0.94	13574
	3.	....	4.80	95.20	.....	1.90	93.16	1.73	2.19	1.02	14729
Lower bench, Freeport coal, New Field mine	1.	1.08	3.20	87.04	8.68	1.30	85.38	1.53	1.94	1.17	13145
	2.	....	3.23	88.00	8.77	1.19	86.31	1.55	1.00	1.18	13289
	3.	....	3.54	96.46	.....	1.30	94.61	1.70	1.10	1.29	14566
Coal below floor, Creighton mine	1.	0.58	1.85	86.44	11.13	1.10	82.38	1.37	0.52	3.50	12938
	2.	....	1.86	86.95	11.19	1.05	82.86	1.38	0.00	3.52	13013
	3.	....	2.09	97.91	.....	1.18	93.31	1.55	0.00	3.96	14653

*(1)—Air dried. *(2)—Moisture free.* *(3)—Moisture and ash free.*

The bone coal underwent part fusion, making a very heterogeneous coke. There were unchanged lumps of shale fused into a mass of very friable coke. The volatile matter ranged from 0.5 to 3.9 per cent, and the ash averaged about 50 per cent. For making coke, the bone coal does not seem to have much value either now or in the near future. Its low heating value (7700 B. t. u.) and high ash content (50 per cent) practically eliminate it from consideration. However, if it were possible to use the coal fairly near its source, and find a use for the ash, the prospects for making it marketable would be much better, and for this the cement industry seems to offer an exceptionally good opening. If the coal makes a satisfactory powdered fuel, and the ash is such that it will permit of good blending with the cement body, an outlet for it in that field is a possibility worthy of further investigation.

According to Bleininger[10], the requirements in a clay for making cement are approximately as follows:

Silica-alumina ratio, 2.9.
Magnesia content, not such as to bring the total magnesia in finished cement above 3 per cent.
Iron oxide, under 6 per cent.
Sulphur, as SO_3, under 3 per cent.

An analysis of the ash from bone coal is given below.

Analysis of ash from bone coal.

	Per cent.
Silica (SiO_2)	60.4
Alumina (Al_2O_3)	30.5
Ferric oxide (Fe_2O_3)	2.9
Titanium oxide (TiO_2)	1.5
Calcium oxide (CaO)	0.4
Magnesium oxide (MgO)	1.2

Ammonia.—By the methods used in these experiments, the true coals yielded from 15 to 20 pounds of ammonium sulphate per ton, while the bone coal and cannel coal gave about half that amount.

Tar oils.—These oils, although from a chemical standpoint the most interesting by-product obtained, were very difficult to analyze and evaluate. This was in part due to their complexity, and in part to the fact that no reliable methods have been devised for the analysis of such oils. Since low-temperature oils differ widely in composition from high-temperature tars, methods ordinarily used for the evaluation of such tars do not apply. Moreover, the quantities of tar oils available in these experiments were not sufficient for the usual tar analysis. Methods used in the analysis of petroleum and oil-shale distillates seemed to fill the requirements better, particularly since low-temperature oils are in many respects similar to shale-oils, and probably will be evaluated on somewhat the same basis in the future. This applies more strictly to the oils from the cannel coals, since there is really no distinct line of demarcation structurally between these coals and oil-shales.

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[10] Bleninger, A. V., Portland cement resources, Illinois Geol. Sur. Bull. 17, 1912, p. 30.

For this investigation, analysis was required to serve a two-fold purpose; first, as a basis for comparing the oils from different portions of the seam, and second, as a basis of evaluation. In this connection it should be remarked that any commercial value assigned to low-temperature tar oils—and shale-oils also—must be provisional, and dependent upon the development of refining methods and market conditions in the future. The fractionation method adopted was essentially the same as that developed by Dean and others[11] for the analytical distillation of crude petroleum, and the fractions were separated into acids, bases, washed oils, and residuals by the usual methods of tar analysis. For this purpose, fractions were so combined as to show the yields of light, middle, and heavy oils of the tar distiller, and the results were also converted by calculation to show yields to be expected by petroleum refining methods.

DEHYDRATION OF TARS.

Before the tars could be fractionated, it was necessary to dehydrate them, and this was a matter which presented considerable difficulty owing to the fact that their specific gravity was near that of water, and accordingly they emulsified very easily. After considerable experimentation, the dehydration method finally adopted was as follows:

The entire tar sample, usually 600 to 700 c. c., was placed in a 1.5 liter copper retort and heated in a Freas automatic drying oven at 115° C. for 24 to 36 hours. The water and light oil vapors driven off were condensed to a 20-inch Liebig glass condenser, and caught in a 200-c. c. graduated cylinder. Here water and oil separated, and the volume of the former was read off directly. The oil was separated and mixed again with the main tar sample after cooling. This method, though slow, required very little attention, and worked out very satisfactorily.

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[11] Dean, E. W., Hill, H. H., Smith, N. A. C., and Jacobs, W. A., Analytical distillation of petroleum, Bureau of Mines Bull. 207, 1922, p. 82.

FRACTIONATION ANALYSIS.

The dehydrated tars obtained in the above manner were fractionally distilled for analysis, the method followed being that of Dean and others previously referred to. Fractions were taken every 25 degrees up to 275° C. at atmospheric pressure. Since a distillation analysis of tar at atmospheric pressure carried beyond 275° C. gives not solely distillation products, but also products formed by cracking, it was decided to use the petroleum vacuum method above that temperature whereby decomposition was avoided. For comparative results in the distillation analyses of low-temperature tars this method can be recommended with the modifications to be mentioned below.

A brief description of the apparatus and method used follows, but for complete details see Bureau of Mines Bulletin 207, previously mentioned. Distillations of 300-c. c. samples were made in a 500-c. c. distilling flask heated by an electrical heater, hemispherical in shape. A circular burner was used to heat the liquid at the surface to destroy any foaming effect. The fractionating column (6½ inches by 1 inch) consisted of an iron jack-chain about No. 18 size, supported in the neck of the flask by a wire held in place with a strip of spring steel. For best results with low-temperature tars, the neck of the flask was wrapped with a thin sheet of asbestos.

The condenser column was practically vertical, 16 inches in length, and was designed to ensure thorough contact of the vapors with the condensing surface. The water-jacket around the condenser was built to allow control of the temperature of the cooling medium. For the lighter condensates, the condenser was packed with ice, but for the heavier ones it was necessary to warm the cooling liquid above the melting points of the distillates, a hot-point immersion heater being used.

The fractions were taken in test-tubes of 30-c. c. capacity, graduated to 0.2 cubic centimeter.

Temperature measurements were made with a mercury thermometer (A. S. T. M. low distillation; 300° maximum). Up to 275° C. the distillation was carried on at atmospheric pressure. At that point the distillation was stopped, and the tars were allowed to cool before starting the vacuum distillation.

The chain fractionating column was removed for the vacuum distillation. For this work, three brass gauze cones were placed in the neck of the distilling flask to prevent the liquid from spraying over into the condenser. One cone was placed at the base of the neck and the two others about 1 inch and 1¼ inches below the exit tube of the flask. The neck was also kept covered with asbestos for the vacuum work.

For the fractionation under reduced pressure a somewhat complicated receiving system was necessary, and the apparatus used in this case was a modification of the Bruhl type, developed by the Bureau of Mines. It consists of a glass jar containing a revolving rack for the graduated test-tubes, and covered with an air-tight lid clamped on with draftman's clamps. The rack revolved by a knob projecting through a stuffing-box. The vacuum regulation at 20 mm. was obtained by equipping the vacuum line with a type of brass "bleed-in-valve" (sleeve-valve vacuum regulator) also described in detail in Bulletin 207.

This particular fractionation method was adopted for two reasons; first, being a well-developed method based on years of experience, it could be applied with confidence; and secondly, it supplied a basis for comparing the coal distillates with those from petroleum and oil-shales. In order to form an idea of what these results would mean to a tar distiller, cuts of 25-degree fractions obtained at atmospheric pressure were combined in table 7 to approximate those ordinarily obtained in tar distillation practice. The vacuum fractions, most of which were greases of about the consistence of vaseline, were added together and treated as lubricating stock.

COMPARISON OF BOILING RANGES OF PETROLEUM, SHALE-OIL, AND CANNEL TAR.

Table 6 shows the remarkably close agreement between the boiling ranges of a Californian crude petroleum, a Utah shale-oil, and a Freeport cannel coal tar. The boiling range of tar from the true Freeport coal does not agree so closely as that of the cannel coal with the shale-oil and petroleum ranges. (See table 5.) This, however, is to be expected, since microscopically there is very little difference between oil-shale and cannel coal. Fine coal structure, however, is very different from that of cannel coal or oil-shale.

It would seem that the cannel coal yields a somewhat better distillate than this particular shale, as judged from the amount and quality of the tops; it gives 44 per cent tops with a 39.5 per cent refining loss, as compared with 34.29 and 43.0 per cent, respectively, for the shale-oil. Further, the shale-oil gives a higher yield of heavy vacuum fractions (43.1 per cent) than the cannel tar (26.7 per cent). The petroleum distillate is, of course, superior to either cannel or shale-oil, but its boiling range lies very close to that of the other oils. As regards the tar acids of the tops, (tables 5 and 6) it may be assumed perhaps that they have some value, whereas the unsaturates are practically valueless, and somewhat troublesome to remove. At least it is an easy matter to remove the acids from the oils by washing with dilute caustic, and they may be recovered from the alkali wash fairly easily if desired. As would be expected, the true coal distillates contain considerably more tar acids than the cannels, and the content of unsaturated compounds is higher in the former case.

In comparing such distillates as petroleum oils, shale-oils, and low-temperature tar oils for the purpose of evaluation, it does not appear that the comparative boiling ranges need be considered, as they are quite similar. The question is largely one of refining loss and the cost of refining. In the case of the shale-oils, the unsaturates only must be removed, and in the case of the tar oils both unsaturates and tar acids must be removed. Petroleum distillates must be refined before being placed on the market, but the loss on refining is almost negligible when compared with that of shale-oils and tar oils. In the case of the latter, recovered tar acids might pay the cost of refining, but would not compensate for the loss of neutral oils entailed by their removal.

Gavin[12] evaluates shale-oil distillates largely according to the amount and quality of tops (fractions boiling under 275° C.) yielded, and his criterion of quality is based on percentage of unsaturated bodies an oil contains. The test for unsaturates consists in washing the oil with sulphuric acid (sp. gr. 1.84) containing 95 per cent H_2SO_4. It is an entirely empirical test, and must not be understood to effect a true separation of all unsaturated hydrocarbons from the remainder of the oil. It does, however, give results comparable with those obtained in refining oil with sulphuric acid, and it therefore furnishes a fair means of comparing similar petroleum and shale-oils. The writers believe that in that sense it applies equally well to low-temperature tar oils. Further, it seems logical to base the evaluation of low-temperature tar oils largely on yields and quality of tops, keeping in mind the value of recoverable tar acids.

COMPOSITION AND EVALUATION OF TAR OILS.

The fractionation results on the dehydrated tars, obtained by the method previously described, are given in table 5.

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[12] Gavin, M. J., Analytical distillations of typical shale-oils: Bureau of Mines Reports of Investigations, Serial No. 2332, 1922, p. 20.

TABLE 5.—*Analytical distillation of low-temperature tars from the Upper Freeport seam.*

Temp. °C.	Air distillation.						Per cent total dry tar by volume.		
	Cannel coal, Frances mine.	Cannel coal, Creighton mine.	Upper bench, Freeport coal, Frances mine.	Upper bench, Freeport coal, NewField mine.	Bone coal, Frances mine.	Bone coal, NewField mine.	Lower bench, Freeport coal, Frances mine.	Lower bench, Freeport coal, NewField mine.	Below floor, Creighton mine.
Up to 50...	0.4	...	...	...	...	...	...	...	...
50- 75...	5.2	0.7	...	0.2	0.4	...	0.1	...	0.5
75-100...	1.7	1.0	0.9	1.3	4.9	1.9	2.1	1.7	1.4
100-125...	1.1	0.6	0.8	1.0	0.0	1.0	0.0	0.6	0.8
125-150...	3.7	1.2	2.5	1.2	1.9	9.3	1.0	1.7	0.4
150-175...	4.8	3.0	3.5	2.8	4.2	3.0	2.7	3.3	2.8
175-200...	6.3	5.5	7.9	9.7	8.6	5.5	10.0	7.5	8.2
200-225...	6.9	9.0	10.9	9.9	7.7	6.6	11.4	11.7	9.4
225-250...	6.2	7.2	6.7	3.3	8.3	7.5	6.3	6.7	5.7
250-275...	7.9	7.6	8.9	8.8	...	5.9	7.6	8.7	7.4
Vacuum distillation at 20 mm.									
Up to 150...	...	...	...	...	0.5	0.6	...	...	...
150-175...	0.4	3.0	0.5	0.3	6.7	1.1	0.6	0.7	...
175-200...	6.1	9.8	3.9	8.0	7.4	3.0	1.4	2.2	2.5
200-225...	9.3	10.0	7.8	8.6	7.4	4.8	4.5	4.9	7.8
225-250...	6.9	9.6	7.3	7.9	9.2	13.2	5.5	6.8	3.6
250-275...	4.0	8.9	6.3	4.6	9.2	6.5	5.6	4.7	4.8
275-300...	...	7.1	6.4	8.9	11.0	7.8	8.0	7.9	8.2
Over 300 pitch...	29.1	25.8	25.7	23.5	12.6	22.8	33.2	30.9	37.5

TABLE 6.—*Boiling ranges of Californian petroleum, Utah shale-oil, and cannel coal tar.*

Temperature, °C.	Petroleum,[a] per cent cut.	Shale-oil,[b] per cent cut.	Cannel tar, per cent cut.
Up to 50..................................	0.1	trace	0.4
50- 75..................................	1.4	0.39	5.2
75-100..................................	2.1	1.58	1.7
100-125..................................	4.4	1.88	1.1
125-150..................................	4.8	3.03	3.7
150-175..................................	4.2	3.83	4.8
175-200..................................	4.5	4.38	6.3
200-225..................................	5.0	5.56	6.9
225-250..................................	5.6	5.62	6.2
250-275..................................	8.2	8.00	7.9
"Tops" to 275° C..........................	40.3	34.27	44.2
Unsaturation of tops (%).................	none	43.0	23.1
Acids in tops (%).........................	none	trace	16.4
Sum, refining loss, tops (%)..............	none	43.0	39.5
Vacuum fractions.			
Up to 200..................................	1.0	3.02	6.5
200-225..................................	6.4	8.56	9.3
225-250..................................	5.5	9.87	6.9
250-275..................................	5.4	10.75	4.0
275-300..................................	6.3	10.90	0.0
	24.6	43.10	26.7
	33.8	22.63	29.1

[a] Dean, E. W., Cooke, M. B.; and Bauer, A. D., Properties of typical crude oils from the producing fields of the Rocky Mountain district: Bureau of Mines Report of Investigations, Serial No. 2235, 1921, 50 pp.

[b] Gavin, M. J., Analytical distillations of typical shale-oils; Bureau of Mines Reports of Investigations, Serial No. 2332, 1922, p. 20.

HEAVY VACUUM OILS.

According to Gluud[18], the heavy oils of low-temperature tars yield excellent lubricants when the tar acids have been removed, and when the residual neutral oils have been purified by steam distillation. Apparently this source of lubricants was largely drawn upon by the Germans during the war. In the United States, however, it appears that such lubricants would fail to compete with those derived from petroleum, since from that source there is an abundant supply and refining is inexpensive. In case of a strong demand for lubricant stock there probably would be a tendency toward the refining of fuel oils and gas oils. Here the tar oils might compete, but they could not have a higher value than that of gas oil. The writers believe that there are two practical ways of utilizing them—namely, either refine only to a slight extent and market as cheap greases, or subject them to a cracking process for the production of motor spirit stock.

LOW-TEMPERATURE TAR OILS FROM THE TAR DISTILLER'S STANDPOINT.

In table 7 the top tar fractions are arranged approximately in accord with those ordinarily obtained in tar distillation prac-

TABLE 7.—*Fractionation analyses of low-temperature tars from coals of the Upper Freeport seam.*

Coal.	Per cent by volume.					
	Light, 0-175° C.	Middle, 175-225° C.	Heavy, 225-275° C.	Total tops, 0-275° C.	Total vacuum fractions, 0-300° C. at 20 mm. pressure.	Pitch above 300° C. at 20 mm. pressure.
Cannel coal, Frances mine..	16.9	13.2	14.1	44.2	26.7	29.1
Cannel coal, Creighton mine	6.5	14.5	14.8	35.8	48.4	15.8
Upper bench, Freeport coal, Frances mine...	7.7	18.8	15.6	42.1	32.2	25.7
Upper bench, Freeport coal, New Field mine	6.5	19.6	12.1	38.2	38.3	23.5
Bone coal, Frances mine...	11.4	16.3	8.3*	36.0	51.4	12.6
Bone coal, New Field mine	15.2	12.1	13.4	40.7	36.5	22.8
Lower bench, Freeport coal, Frances mine...	5.9	21.4	13.9	41.2	25.6	33.2
Lower bench, Freeport coal, New Field mine	7.3	19.2	15.4	41.9	27.2	30.9
Coal below floor, just above fire-clay, Creighton mine..........	4.9	17.6	13.1	35.6	26.9	37.5

*225-250° C.

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[18] Gluud, W., Die tieftemperature verkokung der steinkohle, Wilhelm Knapp, Halle (Salle), 1920.

tice, and the total yields of heavy vacuum distillates and pitches are included. The results show a yield of from 5 to 17 per cent of light oils and from 12 to 21 per cent of middle oils. The heavy oil fractions are not strictly comparable with tar distillers' heavy oils, since the end temperature (275° C.) was low. It is a difficult matter to compare the results of different investigators of low-temperature tars, since analytical methods have not been standardized; and further, the coals from which the results were obtained usually differ widely in character. However, the light oil yields may perhaps be taken as significant. Comparative figures of yields of light oil as determined by several investigators are as follows:

Comparison of yields of light oils.

Investigator	Lewes[a]	Parr[b]	Gluud[c]	Runge[d]	Davis and Berger	Morgan and Soule[e]
Type of coal	Gas coal	Illinois coal		By-product	Freeport by-product	Pittsburgh Terminal
Carbonization method		External and internal	Internal	Continuous, external heating	External heating	Continuous, external heating
Maximum carbonization temperature, °C	400-500	750-800	500	730	600	780
Yield of light oil, per cent of tar	3.10	17.2	13.0	3 gal. per ton on 24 to 30 gal. total tar	6.8	0.64
Maximum temperature of cut, °C	170	210	200	10-12.5%	175	173

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[a] Lewes, V. B., Carbonization of coal: 1912, p. 192.

[b] Parr, S. W., and Olin, H. L., Coking of coal at low temperatures with special reference to the properties and composition of the product: University of Illinois Eng. Exp. Sta. Bull. No. 99, 1915, p. 22.

[c] Loc. cit.

[d] Runge, Walter, Products of low temperature distillation of coal: Chemical Age, vol. 30, No. 1, 1922, p. 9.

[e] Morgan, J. J., and Soule, R. P., Studies in the carbonization of coal: Charactertistics of low-temperature coal tar, Chem. and Met. Eng., vol. 26, No. 20, 1922, p. 23.

The writers are at a loss to explain the low yield of light oils obtained by Morgan and Soule, and strongly disagree with their inference that low-temperature tars have about the same volatility as high-temperature tars. Undoubtedly, exaggerated statements are frequently found in the literature as to the high volatility of low-temperature tar, but certainly work on one tar, regardless of the care taken, does not warrant question of the findings of all previous investigators.

COMPOSITION OF TAR FRACTIONS.

Analysis of the tar fractions, as far as it was practical to carry it out for the purpose of this paper, is given in table 8. It will be seen that the fraction 175 to 225° C. contains the highest percentage of phenolic compounds. In this connection it is also interesting to note the gradual increase in phenolic content (decrease in neutral oils) from the top to the bottom of the seam.

TABLE 8.—*Analyses of light, middle, and heavy oil fractions of low-temperature tars from coals of the Upper Freeport seam.*

(Per cent by volume).

Coal.		Acids. (Soluble 10% NaOH)	Bases. (Soluble 20% H_2SO_4)	Total neutral oils (residue after acids and bases were extracted).	Unsaturated soluble 95% H_2SO_4.
Cannel coal,	1[*]	7.0	1.0	92.0	28.0
Frances mine......	2	28.0	0.0	72.0	27.2
	3	17.0	3.5	79.5	15.5
Cannel coal,	1	8.3	0.0	91.7	27.5
Creighton mine....	2	18.0	1.0	81.0	26.5
	3	13.0	0.0	87.0	24.0
Upper bench,	1	16.0	0.0	84.0	35.3
Freeport coal.	2	42.0	2.0	56.0	31.4
Frances mine......	3	34.3	6.4	59.3	22.2
Upper bench,	1	12.8	0.7	86.5	37.2
Freeport coal,	2	38.2	0.6	61.2	29.4
New Field mine....	3	25.3	0.3	74.4	42.6
Bone coal,	1	13.0	1.0	86.0	18.5
Frances mine.....	2	46.5	4.2	49.3	12.7
	3	30.5	3.0	66.5	18.2
Bone coal.	1	16.2	0.0	83.8	18.7
New Field mine....	2	46.0	0.5	53.5	14.0
	3	28.3	3.0	68.7	21.3
Lower bench,	1	15.4	0.0	84.6	79.2
Freeport coal,	2	48.0	0.0	52.0	32.5
Frances mine......	3	33.0	4.0	63.0	21.0
Lower bench,	1	16.6	1.0	82.4	43.6
Freeport coal,	2	49.5	0.7	49.8	21.5
New Field mine...	3	35.0	5.0	60.0	19.0
Coal below floor just	1	18.8	1.3	79.9	61.3
above fireclay,	2	60.0	2.5	37.5	24.0
Creighton mine....	3	33.0	6.0	61.0	24.0

[*] *1—Light oils (0–175°)*
2—Middle oils (175–225°)
3—Heavy oils (225–275°)

The amount of bases is variable, and shows no consistent variation with the character of the coal. Cannel and bone coal distillates consistently show less unsaturation than the true coals; a difference between the true coal fractions in this respect cannot be claimed. Table 9 gives the specific gravities of the several tar fractions as obtained by the Westphal balance at 15.5° C. It will be noted that the general tendency is toward an increase in gravity from the top to the bottom of the seam.

IMPORTANCE OF MICROSCOPIC ANALYSES OF COAL.

It is well known that chemical analysis alone gives meager information on which to base predictions as to the character of by-products yielded and coking qualities of a given coal. Reinhardt Thiessen[14], of the Bureau of Mines, and A. W. Voorhees, formerly therewith, however, developed a method of analysis based on microstructure of coals which the writers believe is destined to throw considerable light on the problem. For example, they have found that there is a gradation in properties from the top to bottom of this particular seam. The top partings contain a large percentage of attritus[15] (spore matter and degradation products), while the lower partings are high in anthraxylon (woody matter). From previous experience, and from a consideration of what is known chemically of anthraxylon, it is logical to expect a preponderance of tar acids in distillates from that body. Cannel coal, which is largely spore matter, should yield a small amount of

TABLE 9.—*Specific gravities of the light, middle, and heavy oils from low-temperature Freeport coal tars.*

(At 15.5° C.)

Coal.	Light, 0-175° C.	Middle, 175-225° C.	Heavy, 225-275° C.
Cannel coal, Frances mine	0.820	0.889	0.910
Cannel coal, Creighton mine	0.811	0.862	0.879
Upper bench, Freeport coal, Frances mine	0.851	0.944	0.983
Upper bench, Freeport coal, New Field mine	0.843	0.939	0.980
Bone coal, Frances mine	0.836	0.941	0.954
New Field mine	0.846	0.955	0.964
Lower bench, Freeport coal, Frances mine	0.864	0.966	0.995
Lower bench, Freeport coal, New Field mine	0.852	0.953	0.982
Coal below floor, just above fireclay, Creighton mine	0.881	0.976	1.008

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[14] Thiessen, Reinhardt, and Voorhees, A. W., Microscopic study of the Freeport coal bed, Pennsylvania; Bull. 2, Carnegie Inst. of Technology, 1922.

[15] Thiessen, Reinhardt, Compilation and composition of bituminous coals. Jour. Geology, vol. 28, No. 3, April-May, 1920, p. 185.

acids and a large amount of neutral oils, and this was found to be the case. As for the true coals of this seam, however, the problem was somewhat complicated by the fact that both benches were really a mixture of attritus and anthraxylon, the latter predominating in the lower bench. Other papers now in the course of preparation will bring out more clearly the micro-analysis of this seam and its bearing on by-products.

ECONOMIC VALUE OF BY-PRODUCTS.

Inasmuch as it is impossible to discuss fully within the limits of this paper the economic factors involved in the production and refining of oils from the low-temperature carbonization of coals, a more general view of the situation will be taken. Such factors as market, plant site, labor, etc., would, however, determine the feasibility of low-temperature carbonization, and would require careful consideration before attempts could be made in the commercial development of a low-temperature industry.

Oils.—Petroleum, as the source of motor fuel, lubricants, illuminating oils, and fuel oils, has never had a rival; and with the great number of potential foreign oil fields which have yet to be exploited, petroleum is not very likely to be superseded for some time as the source of these products. Nevertheless, the great annual increase in the demand for fuels for internal-combustion engines will probably in the near future permit profitable competition in this field by distillation products of oil-shales and coals. Even at this time, benzols from high-temperature carbonization processes find an outlet in this field, although careful refining is necessary to make them suitable. In this respect it is likely that oils from the low-temperature coking processes of coal would be able to compete with petroleum before shale-oils on account of the valuable marketable coked residues. The distillation residues from oil-shales have little or no commercial value at present, while the coal residues, often without any modification, are fuels comparable to anthracite coal.

The gases, too, from coal, are better in quality and greater in quantity than those from shales.

As a source of wood preservatives, low-temperature tars are very important. It has been said[16] that such low-temperature tar acids are more suitable for preservatives than those now used. Cattle dip is also an outlet for these products.

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[16] Coffin, F. P., Uses for low temperature tar oils, Gas Age Record, vol. 48, No. 3, August 6, 1921, p. 97.

Regarding the possible derivation of lubricants from the oils, it seems highly improbable that such an extraction can be profitably made for some time, owing to the amount of refining necessary. The petroleum industry, by further refining some of its materials now going out as fuel oils, could easily and efficiently keep up with any increase in demand for lubricants likely to arise in the near future.

Coked residue.—The coked residues of the true coals were intermediate in properties between semi-coke and metallurgical coke, approaching the latter closely. The writers believe that they would serve as foundry cokes. The residues from the waste cannels and bone coals would serve no industrial purpose where coke is now required. There is a possibility that it would be practical to use them pulverized as fuel for cement kilns; or they might be used in producers generating gas to heat carbonizing retorts. In either case their fuel content, pound for pound of combustible, would approach the worth of that of coke.

Gas.—The gas, although the yields (7,000 to 8,200 cubic feet per ton of coal) were low, was equal in quality to any artificial gas made, excepting oil-gas. Gases from cannel coal were exceptionally good, while those from bone coal were good enough for domestic use.

COMPARATIVE VALUE OF BY-PRODUCTS.

From time to time, estimates of the value of low-temperature by-products have appeared in the technical press, and it would seem that such estimates have been for the most part somewhat extravagant. In presenting the rough estimate shown in table 10, chiefly for the purpose of comparing the different seam partings, the writers have tried to be conservative, and desire to express the hope that they have erred in being too conservative. Frank criticism by chemists and engineers directly interested in any phase of this important subject is solicited, since it is only through free interchange of ideas among experienced men that reliable information can be compiled. It is believed entirely practical to assemble and publish such information in the interest of conservation of our national resources, with the kind co-operation of interested readers. This is what the writers hope to accomplish.

Under present economic conditions it probably would not pay to carbonize Freeport coal at low temperatures, as far as can be determined by the foregoing experiments. The waste coals,

TABLE 10.—*Comparative values of by-products from constituents of the Freeport coal seam.*

(Per ton of coal coked at 600° C.)

By-product.	Upper bench, Freeport coal.	Lower bench, Freeport coal.	Cannel coal.	Bone coal.
Coked residue	68% of $4 = $2.72	69% of $4 = $2.76	75% of $4 x 9/13 less 50% = $1.04	79% of $4 x 7/13 less 50% = $0.85
Gas	7,000 cu. ft. @ 20¢ = 1.40	8,000 cu. ft. @ 20¢ = 1.60	4,000 cu. ft. @ 20¢ = 0.80	3,500 cu. ft. @ 20¢ = 0.70
Top oils to 275° C.	10.8 gal. @ 10¢ = 1.08	10 gal. @ 10¢ = 1.00	12.3 gal. @ 10¢ = 1.23	5.3 gal. @ 10¢ = 0.53
Lubricants or gas oils	8.1 gal. @ 6¢ = 0.48	6.2 gal. @ 6¢ = 0.36	8.1 gal. @ 6¢ = 0.48	5 gal. @ 6¢ = 0.30
Ammonium sulphate	18 lb. @ 4¢ = 0.72	18 lb. @ 4¢ = 0.72	9 lb. @ 4¢ = 0.36	9 lb. @ 4¢ = 0.36
Soft pitch	6.5 gal. @ 2¢ = 0.13	7.8 gal. @ 2¢ = 0.15	6 gal. @ 2¢ = 0.12	2.4 gal. @ 2¢ = 0.09
Total value of products	$6.53	$6.59	$4.03	$2.83

however, clearly have a value when considered from the low-temperature standpoint; and it may perhaps be assumed that there would be a fair margin of profit between mining and distillation costs and the market value of by-products.

SUMMARY.

Samples from all partings from the thick Freeport seam in two representative mines were destructively distilled at temperatures not in excess of 600° C., and the by-products were collected, analyzed, and evaluated as far as was practical. The roof of the seam consisted of cannel coal and directly below this was the upper bench Freeport coal. A parting of bone coal 6 to 12 inches thick separated the upper bench coal from that of the lower, and underneath the lower bench, separated therefrom by a thin parting of slate, was a strata of about 12 inches of true coal. The bone, cannel, and sub-floor strata are not mined as a rule. These, as well as the coals of the upper and lower benches, were distilled and the distillation products were compared, with the following results:

The upper and lower benches of Freeport coal and the sub-floor strata as well yielded from 67 to 69.5 per cent of low-volatile coke, approximating by-product coke in properties. Tar yields varied from 23½ to 28 gallons per ton of coal, and gas yields varied from 7,175 to 8,360 cubic feet per ton of 662 to 728 B. t. u. gas. The tars yielded from 38 to 42 per cent tops boiling under 275° C., 25 to 32 per cent vacuum oils boiling under 20 millimeter pressure up to 300° C., and 23.5 to 37.5 per cent of soft pitch. The tops are looked upon as motor spirit and solvent stock, and the heavy oils are considered as gas oils, or with refining, as lubricants.

The cannel coals yielded 74.7 and 78.2 per cent of non-fused residue containing about 35 per cent ash, 27½ to 33½ gallons of tar oils, and 3,800 to 4,500 cubic feet of gas per ton. The oils analyzed 35.8 and 44.2 per cent tops, 48.4 and 26.7 per cent vaccum oils, and 15.8 to 29.1 per cent soft pitch. The boiling ranges of the tars were very similar to those of samples of petroleum and shale-oil fractionated by the same method. The cannel oil was superior to the shale-oil, but of course, not so good as the petroleum oil.

The bone coals yielded 78.2 and 79.5 per cent of semi-fused residue, containing 50 per cent ash, 13 and 14 gallons of tar, and 3,400 to 3,600 cubic feet of gas per ton. The quality of the tar did not differ greatly from that of the true coal.

The true coals yielded from 15 to 20 pounds of ammonium sulphate per ton, and the bone and cannel coals about half that amount.

In view of the information furnished the writers by Thiessen and Voorhees, on the microstructure of the Freeport seam, it is clear that coals rich in anthraxylon (woody matter, bright coal) give high gas yields and tars high in phenolic or acid bodies. The pitch content of anthraxylon tars is noticeably higher than that from attritus (dull coal) tars, whereas the heavy oil yield was highest for the attritus tars. The true coal cokes obtained in these experiments showed no distinguishable variation with microstructure. This, however, may have been due to the fact that in none of the samples was a great preponderance of attritus or anthraxylon present; they were varying mixtures of the two constituents.

CONCLUSIONS.

From the data obtained in this research the following conclusions can be drawn:

1. Thick Freeport coal when carbonized at temperatures around 600° C. will yield 25 to 30 gallons of tar, 8,000 cubic feet of gas, and about 1,380 pounds of low-volatile coke per ton. The yield of ammonium sulphate is from 15 to 20 pounds per ton.

2. Bone coal is worth about half as much as the true coal—that is, from the standpoint of gas and oil yields. The distillation residue is not a coke and is of small value, but perhaps could be utilized for special purposes.

3. The cannel coal tar is worth perhaps more than the tar from the true coal, and the gas is better, though the yield is only about half that of the true coal. The residue is non-fused, different from that of the bone coal, and lower in ash content.

4. Bone coals and cannel coals yield about half as much ammonium sulphate as the true coals.

5. Considering the value of thick Freeport coal as a high-temperature by-product or gas coal, it probably would not pay under prevailing economic conditions to carbonize it at low temperatures.

6. Low-temperature carbonization of the waste coals of the seam appears economically feasible; successful utilization of the

distillation residue is an important factor on which further investigation is required.

7. By-products from coals of this seam show definite variation in character with variation in microstructure of the coals. Micro-analysis probably is destined to be of great value in determining the suitability of coals for by-product treatment.

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CRAMER, CRAFTON

Bulletin 2

COAL-MINING INVESTIGATIONS

UNDER AUSPICES OF

CARNEGIE INSTITUTE OF TECHNOLOGY,
UNITED STATES BUREAU OF MINES,
ADVISORY BOARD OF COAL-MINE OPERATORS
AND ENGINEERS.

A MICROSCOPIC STUDY OF THE FREEPORT COAL BED, PENNSYLVANIA.

By

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and

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CARNEGIE INSTITUTE OF TECHNOLOGY,
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PREFACE.

Pittsburgh is the greatest industrial center in America, and the heart of the greatest bituminous coal-mining district in the world. It is eminently desirable, therefore, that this city should have an institution which devotes a part of its great facilities to the scientific study of that branch of the industry which is largely responsible for Pittsburgh's development and that of western Pennsylvania.

On May 27, 1919, a number of the leading representatives of the coal-mining industry of western Pennsylvania met in conference with the then President of the Carnegie Institute of Technology with a view of bringing about closer relations between the Institute and the mining interests. It was felt that the advice and cooperation of men in the field were necessary for the training of young men for mining work, and at the conclusion of the meeting the following resolution was adopted:

> That this gathering give its approval and moral and material support to the form of education proposed for the Carnegie Institute of Technology by which students may receive a combined technical, practical, and business training, necessary to fit them for service in the coal mining and allied industries. Further, that the President of the Carnegie Institute of Technology appoint a board of no less than ten men representing the coal mining and allied industries, the United States Bureau of Mines, the State Department of Mines, and the Carnegie Institute of Technology, who will advise and assist in carrying out this program of education and training, particularly in its practical phases in the mining industry and in its cooperation with the United States Bureau of Mines.

Following further the intention of this resolution, the President of the Institute entered into a cooperative agreement on June 1, 1919, with the Director of the United States Bureau of Mines whereby full advantage could be taken of the Bureau's laboratories, equipment, and library, as well as of the advice and instruction of its technical staff.

To carry out this new program there was organized during the summer months the Cooperative Mining Courses in the Department of Mining and Metallurgical Engineering, College of Engineering, of the Institute. The course in mining engineering covers four years, and leads to the degree of Bachelor of Science. The two-year course in coal mining is planned to prepare men with a certain amount of practical experience for executive positions. The four-weeks intensive summer course in coal mining is designed for miners who aspire to be firebosses and mine foremen. In a large measure, the new mining, ore-dressing, and coal-washing laboratories at the Institute have been equipped gratuitiously by various manufacturers of mining machinery and appliances. Cooperative research through teaching and research fellowships is devoted to various problems in coal mining and the utilization of fuels. The Institute selects the fellows; the Bureau of Mines provides the laboratory facilities; and the Advisory Board determines what problems be undertaken, and publishes the reports.

The primary object of this cooperation of the Carnegie Institute of Technology, the United States Bureau of Mines, and the Advisory Board of Coal Mine Operators and Engineers, is the proper education and training of young men for the mining industry. The ultimate objective is to bring about better conditions and greater efficiency in mining operations. The decrease in reserves of coal and increasing cost of production make it urgently necessary for mine operators and engineers to take advantage of everything which modern science, machinery, and methods can contribute.

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FOREWORD.

The microscopic study of the Freeport coal bed, Pennsylvania, was undertaken, with the approval of the Advisory Board of coal operators, for the purpose of obtaining accurate data on the structure of the various layers or benches of coal comprising the Freeport coal bed, and the correlation of this data with the yields of oils, tars, gas and coke obtained from those same sections of the Freeport coal bed by destructive distillation, as described in Bulletin 1 of this series, entitled "The Yield and Quality of the Gas, Oil and other By-Products of the Constituents of the Freeport Coal Bed," by J. D. Davis and H. G. Berger.

The thick Freeport coal bed was sampled at five mines, suitably situated in the area under consideration. Photomicrographs were made at regular intervals from the bottom to the top of the bed, including the bone and cannel constituents, and a number of the typical photomicrographs are reproduced in this report.

The investigation showed that the structure of the Freeport bed varies vertically, but not horizontally; that the lower benches are rich in anthraxylon the proportion of which diminishes towards the top of the bed, ending finally in a layer of cannel coal made almost wholly of attritus.

The attritus is rich in oil and tar-producing constituents.

The spore-exines of the Freeport bed are characteristic, and sufficient data have been obtained whereby the identity of this bed can be established in other localities by microscopic examination.

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A MICROSCOPIC STUDY OF THE FREEPORT COAL BED, PENNSYLVANIA.

By REINHARDT THIESSEN *and* ANSON W. VOORHEES.

INTRODUCTION.

For many years, geologists, paleobotanists, engineers, and chemists in the United States and abroad have been studying coal in its various forms, and have amassed much information therefrom; but there are still many problems which have either not been worked on at all or which have never been solved. In fact, the problems offered for research on coal and its products are more numerous today than before, for as the work has advanced, the number and diversity of the problems has increased. So today, if an investigator is to make progress in this field, he must choose a specific problem in this field of research.

The investigation that formed the basis of this report is a very small part of the general program of research which is being carried on to obtain a better knowledge of the origin, composition, nature, and chemistry of coals in general. Some of the more specific aims of this problem are (1) to determine whether a coal seam varies in composition either vertically or horizontally, or if it is of uniform composition throughout; (2) to discover uses for those sections of the seam which are now being discarded; and (3) to try to find the relationship between the various constituents of the coal and the products obtained by coking.

HISTORICAL REVIEW.

Before one can intelligently discuss the constituents of coal it is advisable to review briefly the work of previous investigators. Although research in coal dates back to a very early date, it will be sufficient for this paper to review the period since the year 1831, the year when the microscope is first reported to have been employed in coal investigations.

Witham[1] was the first to investigate coal by the use of thin sections. He found and illustrated what he believed to be the cellular tissue of vascular plants, but which was probably cross sections of spores.

Link[2] differed with Witham inasmuch as he found no wood structure except in the charcoal.

Goppert[3] made a study of the plant remains which he found in the charcoal and in small cleavage surfaces, but apparently did not work on thin sections.

In a comparison of cannel coal and Torbane Hill mineral, Queckett[4] pointed out the woody structure in cannel coal, but his "cells" and "fibers" were probably only cross sections of spores and thin woody layers of coal.

This same error was noted by Balfour[5] who called the same objects "spaces" and "cavities."

Dawson[6] seems to have been the first to realize that coal is made up of compact coal and mineral charcoal, and that the former is again divided into bright coal which he believed came from the bark of Sigillaria and allied plants; and dull coal which he supposed to have been derived from molds and herbaceous plants. He used thin sections, but did not base his conclusions on them, because the sections were probably too thick to show all structure.

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[1] Witham, Henry, On the general result of botanical investigation concerning the character of the ancient flora which by its composition has furnished the material of coal seams; Rept. 1st and 2nd meetings British Assn. Avd. Sci., 1831 and 1832, p. 78; On fossil vegetation: Rept. 1st and 2nd meetings British Assn. Adv. Sci., 1831 and 1832, p. 578. Bonnie, James, and Kidston, Robert. On the occurrence of spores in the carboniferous formation of Scotland: Proc. Roy. Phys. Soc. Edinburgh, vol. 9, 1885-1888, pp. 82-117.

[2] Link, Frederick, Ueber den Ursprung der Steinkohlen und Braunkohlen nach mikroskopischen Untersuchungen: Abhandl. K. Akad. Wiss, Berlin, 1838, pp. 33-34.

[3] Goppert, H. R., Uber die Verbeitung der fossilen gewachse in der Steinkohlen formation: Schlesische gesell. Ubersicht, 1840, pp. 74-77: Uber die Holzarten in den braukohlenartigen Ablagerungen: Kartstens Archiv., Bd. 18, 1844, pp. 527-529: Uber das verhaltniss der Boghead parrot cannel-coal zur steinkohle: Dingl. poly. Jour. Bd. 145, 1857, pp. 212-217: Ablandlung, eingesandt als Antwort auf die Preisfrange—"Man suche durch genaue Unter suchungen darzuthun, ob die Steinkohlenlager aus Pflanzen entstanden sein, welche an den Stellen, wo jene gefunden werden, wuchsen oder ob diese Pflanzen an anderen Orton lebten, und nach den Stellen, wo sich die Steinkohlenlager bifinden Hingefurt wurden:" Nat. Verh. Monatschr., Bd. 4, 1848, pp. 1-298.

[4] Queckett, John, On the minute structure of a peculiar combustible mineral from the coal measures of Torbane Hill, near Bathgate, Linlithgowshire, known in commerce as Boghead cannel coal: Trans. Micros. Soc. London, vol. 2, 1853, pp. 34-66.

[5] Balfour, J. H., On certain vegetable organisms found in coal from Fordel: Trans. Roy. Soc. Edinburgh, vol. 21, 1854, pp. 187-193.

[6] Dawson, J. W., On the vegetable structure in coal: Quart. Jour. Geol. Soc., London, vol. 15, 1859, pp. 626-641; On the conditions of the deposition of coal, more especially as illustrated by the coal formation of Nova Scotia and New Brunswick: Quart. Jour. Soc. London, vol. 22, 1866, pp. 95-169.

Williamson[7], after long investigation, recognized the compact or more bituminous coal as well as the charcoal. He found woody structure in the charcoal only, and believed the compact coal to be of a very different character. He considered that this compact coal was made up of a general matrix, which he called "brown plasm," mixed with spore-exines.

Von Guembel[8] made a very careful and exact study, and it is from his work that our present conception of the composition of coal has been largely derived. He did not use thin sections, but was very successful in using and interpreting the results of Schulze's[9] maceration process. Through this process he became convinced that coal is made up of alternating layers of "glanz" or "bright coal" and "dull coal," having occasional bands of charcoal between them. In the glanz coal he found only a little evidence of plant structure, but in the dull coal he found a great deal. His work was very painstaking, and his careful identification of a number of cells and plant constituents has proved of great value.

Potonie[10] divided coal into three classes which he called sapropellic, humic, and liptobiolithic. He believed them to have been formed respectively from plant and animal organisms; true land plants which live under moist conditions; and through the decay of land plants rich in resin, resin-waxes, or waxes from which the humic matter had disappeared. These three kinds of components were supposed by him to make up the alternate layers of coal.

Lomax[11], in describing the laminations of coal, believes that the dull layers are composed of megaspores embedded in a ground mass of microspores. He supposes that the bright layers are made up of microspores in a groundmass leaf and plant tissue which has been highly compressed. Lomax concludes that there is little of the vascular or woody matter preserved except in the charcoal.

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[7] Williamson, W. C., Preliminary remarks on the microscopic structure of coal: Rept. British Assn. Adv. Sci., 1881, pp. 625-626.

[8] von Guembel, C. W., Beitrage zur Kenntniss der Textur verhaltnisse der Mineralkohlen: K-b. Akad. Wiss. Munich, Sitzungber. Math. Phys. Klasse, Bd. 13, 1883, pp. 111-216.

[9] Schulze, Franz, Ueber das Vorkomen wohlerhaltenes cellulose in Braunkohle und Steinkohle: Sitzungsber. K. preuss. Akad. Wiss. Berlin, 1855, pp. 676-678.

[10] Potonie, H., Klassification and Terminologie der rezenten brennbaren Biolithe und ihre Lagerstadte: Abhandl. K. geol. Landessantalt, Bd. 48, 1906; Die Enstehung der Steinkohle und der Kanstobiolithe Uberhaupt, wie des Torfes, der Braunkohle, des Petroleum, u. o. w., 1910.

[11] Lomax, James, The microscopic examination of coal and its use in determining the inflammable constituents present therein: Trans. Inst. Min. Eng., vol. 42, 1912, pp. 2-21.

White and Thiessen[12] were the first to interpret the different laminae in the coal. They conclude that the bright bands represented what were once the trunks, branches, and stems, or parts thereof, which are now much compressed and coalified. The dull bands are made of thin bands of "bright coal" and attritus composed of spore-exines, pollen-exines, and the general woody degradation products. The attritus corresponds very closely to the black mud of peat. This forms the groundmass for the woody matter.

Stopes[13] divides coal into four constituents as follows:

1. Fusain—the equivalent of "mother of coal," "mineral charcoal," etc.

2. Durain—the equivalent of "dull" hard coal, the Mattkohle of the Germans, etc.

3. Clarain—together the equivalent of "bright" or glanz coal of various investigators, the "glanzkohle" of the Germans. Sometimes the "bright" coal of one investigator seems to be vitrain only.

4. Vitrain—coal with a concoidal fracture, brilliant in appearance.

PRESENT DAY KNOWLEDGE OF COAL.

A large block or chunk of bituminous coal is readily seen to be stratified and composed of various layers and sheets of coal, which differ from one another in color, texture, and fracture, varying greatly in thickness.

Most writers describe two kinds of constituents in the coal, namely, mineral charcoal or mother of coal, and the compact coal. The former, although conspicuous, comprises but a small part of the whole, while the latter forms the largest part of the coal.

The compact coal usually shows two kinds of alternating and sharply contrasting layers, which are easily recognizable. One is jet black, highly lustrous, and has a concoidal fracture if broken, while the other is grayish in color, less compact, lacks luster, and has an irregular fracture. The former has been variously called "bright coal" or "glance coal," and the latter "mat coal" or "dull coal." On careful examination the "bright coal" is found to occur as more or less lens-shaped masses of varying size embedded in dull coal.

---

[12] White, David, and Thiessen, Reinhardt, Origin of coal: Bureau of Mines, Bull. 38, 1914, 390 pp.

[13] Stopes, Marie C., On the four visible ingredients in banded bituminous coal. Studies in the composition of coal, No. 1, Proc. Royal Soc., B., vol. 90, 1919.

If the dull coal be examined carefully, it will be found to be laminated; and these laminae again consist of small lenses of bright coal embedded in dull coal.

The sample of Illinois coal illustrated in Plate I is representative of most bituminous coals. In this lump the bright coal appears as rather uniform black bands (*a*), and the dull coal is represented by the finely striated lighter colored bands (*b*). This is typical of all ordinary bituminous coals, although in some, one constituent is more abundant than in others.

That bright coal or anthraxylon (from the Greek *anthrax*, coal, and *xylon*, wood) has been derived from wood or the woody parts of plants can easily be shown by the microscopic study of thin sections. Cell structure and woody fiber are always more or less plainly evident, and this structure is so well preserved as to leave no doubt that the anthraxylon represents the remains of the woody portions of the plants.

It has already been stated that the dull coal is composed of thin strips of anthraxylon embedded in an attritus and, therefore, we may consider the dull coal as consisting of an embedding material or attritus with small bits of anthraxylon in it. In horizontal cleavage surfaces, small patches of woody material are apparent. If these woody-looking patches be scratched with a sharp tool, the bright glistening anthraxylon is immediately apparent, showing that these patches are not merely casts, but are really the bits of woody matter that were in the peat bog and which have been transformed into anthraxylon. This makes it evident that the woody patches in the horizontal and the glistening band seen in the vertical sections are identical. This has been proved by correlation of opaque and transparent sections, also by the use of Schulze reagent. These small anthraxylon patches are traceable to the scaly chips of wood and comparable to small twigs and chips found in the peat.

In the coal can be found almost all of the different kinds of plant tissues, but we find, as might be expected, a predominance of the decay-resisting parts of the plants. Among these might be mentioned, besides the woody tissue, cuticles which are often apparent in thin sections as long wavy strips—sometimes having serrated edges—spore-exines and resins.

The attritus, as seen in sections under the microscope, is made up of cellulosic degradation products or humic matter, spore-exines, resinous matter, cuticular matter, and more highly carbonized material. The humic matter consists of cellulosis degradation products more finely divided than the smaller anthraxylon pieces, but exclusive of resinous, cuticular, spore, or carbonaceous matter. It is true, however, that the humic matter is not a vague plastic or homogeneous mass, but most of it can be resolved into individual particles under the highest powers of the microscope. Even in the small part which appears homogeneous under the ordinary high powers of the microscope, and approaches the colloidal state, proper methods will show that it really consists of individual particles.

The spore-exines are always present, no coal so far examined being entirely free of them. These bodies are most conspicuous under the microscope on account of their transparency and reddish or yellow color.

In vertical sections at low magnification, they appear as small linear, dumb-bell, or platter-shaped patches; but at high magnification, when whole, they look like flattened rings, being really collapsed spheres. These represent the shells or spore-walls or exines of the spores of Paleozoic plants.

The spore-exines can best be studied by the maceration process with the aid of Schulze reagent. From these studies, spore-exines of several different species and genera of plants have been observed, and these plants have all contributed to the formation of the coal. In horizontal sections, the tetra-sporic mark is often very clearly shown and is characteristic of the spore-exines.

The exines of pollen grains often exist in large numbers, and are distinguishable by the slit running parallel to the long axis of the oval, having frequently a short cross slit at or near one end of the longitudinal slit. The tetra-sporic mark is never found in these pollen-exines. They are similar in appearance to the spore-exines, but always have a smooth surface with no hairlike covering or spines.

The resinous matter is scattered throughout all coals, and appears under the microscope as more or less rounded masses which appear perfectly homogenous or vitreous in consistence. The color of these particles varies from almost colorless to a deep red or brownish red.

In almost all sections, black patches of irregular shape are found, and these represent the more highly carbonized portions of the coal. Some show very definite plant structure, while others show no structure whatever, and are of undetermined origin. These patches are almost opaque, but in the thinnest parts sometimes appear dark red, or even yellow. The more highly carbonized constituents of the attritus is merely mother of coal in a finely divided condition. In fact, no line of distinction can be drawn between these and the larger components so easily noticed as mother of coal.

A summary of the more important facts should be kept in mind. Ordinary bituminous coals are essentially composed of anthraxylon, which is that part of the coal derived from the woody or cellulosic constituents of plants, such as fragments of stems, branches, twigs, and roots. These have undergone a process of decay, putrefaction, and coalification, resulting in the wood losing much of its mass, having been compressed and transformed into flat, lenticular, jetty masses, popularly known as "bright coal."

During the period of decay and putrefaction—that is, during the peat stage—more or less of the plant matter was macerated through the agencies of decay and attrition and reduced to a mud or ooze, called the "attritus." It consists of all kinds of plant products. Having been formed by decay and putrefaction, it includes many of the more resistant plant products such as spores, cuticles, resinous matter, waxes, gums, and the like.

The pieces of anthraxylon are embedded in the attritus, and the relative quantities of these components and constituents vary in different coal beds. A coal may be composed largely or almost entirely of anthraxylon, and contain very little attritus. Such a coal is called an "anthraxylous coal." Or a coal may be composed largely of attritus and contain relatively little anthraxylon, in which case it is called an "attritious coal." When a coal is composed entirely or very largely of attritus, it becomes a "cannel coal." Between these two extremes all stages of inter-graduation may be found.

EXPERIMENTAL WORK.

Preparation of thin sections.—The most satisfactory method for the microscopic study of coal is the use of thin sections, as by this means the coal is seen in its original chemical and physical state, with the natural colors preserved. The coal remains in its original condition, except that it is ground thin enough to be transparent, and to allow photomicrographs to be taken at magnifications as high as 2,000 diameters.

A piece of solid coal about ¾ inch square was found to be about the right size for preparation. The surface selected for the section was ground down to a perfect plane. For cross sections the grinding was done at right angles to the bedding plane; while for horizontal sections the grinding should be as nearly parallel as possible to the bedding plane. This grinding was done on a fine carborundum lap, using water and abrasive powder for the coarse grinding, while the fine grinding was done on the same lap without the abrasive. The surface was then smoothed by hand on a very fine hone which was kept under a stream of water. The hone had to be kept perfectly clean, and this was best done by rubbing it with a good grade of rubber pencil eraser or a "rubber" usually furnished with "bluestone" hones. If a higher polish was desired than could be obtained on the fine hone, the dry surface was carefully rubbed on a leather block strop.

When the surface was properly polished, the block was soaked for a few minutes in paraffin heated to about 105° C. to waterproof the prepared surface.

The prepared block was wiped free from superfluous paraffin, and the piece of coal and an object slide with a little cement on it were placed in a drying oven at 105° C. until the cement was melted and free from bubbles. The cement was made of three parts of Canada balsam and two parts of marine glue heated to 105° C. (The cement should be of such a consistence that it will be hard, but not brittle, when cold). The coal was pressed with a clamp onto the slide, taking care that no bubbles remained between the surfaces. It was then allowed to cool slowly to room temperature.

After the prepared slide had cooled, the clamp was removed and the coal was ground down as thin as possible on the lap, the procedure being the same as in preparing the plain surface. After carefully washing off all abrasive powder and dust, the section was rubbed down to transparency on the hone, great care being taken to rub in only one direction and keep the hone free from all dust and grit. The grinding is very difficult, but if care is taken, sections can be reduced to four or five microns in thickness (1 micron = 1/1000 millimeter, or 1/25,000 inch).

THE THICK FREEPORT SEAM.

Geographic.—The thick Freeport coal bed[14] is a phenomenon caused by an unusual thickening of the Upper Freeport bed, ranging from 5 to 11 feet in thickness in a proved area about 15 miles long by 8 miles wide, which is almost bisected by the Allegheny River, and contains 75,000 acres in Allegheny, Westmoreland, and Butler counties. The northern boundary of this area lies 10 miles northeast of Pittsburgh. Detached areas are reported to have been found at Wilmerding and in the neighborhood of Saltsburg, which would indicate a much greater area for this thick coal.

Stratigraphic.—The Freeport bed is in the Allegheny formation of the Pennsylvania series of the Upper Carboniferous system.

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[14] Coal Catalog, 1922, p. 706, Keystone Cons. Pub. Co., Pittsburgh, Pa.

It is generally overlain by the Mahoning sandstone and below it is the Freeport sandstone.

Mines sampled.—In order to cover the area as well as possible, five mines were selected, widely enough distributed over the territory to be representative of this seam. These mines were: The Oakmont No. 1 mine of the Diamond Coal & Coke Co. at Barking Station; the Parnassus mine of the Valley Camp Coal & Coke Co., at Parnassus; the Indianola mine of the Inland Collieries Co., at Indianola; the New Field mine of the New Field By-Product Coal & Coke Co., at Piercedale; and the mine of the Pittsburgh Plate Glass Co. at Creighton.

Throughout the area the seam shows the same general characteristics, and stratigraphically it is much the same in the five mines which were investigated. So instead of giving the exact thickness of each component of the seam in each mine, one typical columnar section will be described.

Forming a floor for the bed is a variable deposit of fireclay, of a light gray color and fine texture. For the most part it is very compact, and is about as hard as the shale layers.

A band of coal varying in thickness from about 2 to 6 inches lies immediately on the fireclay. It is a very compact firm coal having a high luster. Even in a macroscopic examination, the anthraxylous nature of this layer is very evident. (See Plate II.)

Over this layer of coal is a layer of shale, called "binder," very similar to the one above, but richer in pyrite. (See Plate II.)

Above this shale is another layer of coal usually about 3 or 4 inches in thickness. (See Plate III.)

Above this layer of coal there is a band of compact bituminous gray shale about one inch in thickness, called the "brick bottom." In this band there are many bits of shiny anthraxylous-looking matter. The thickness of the band varies from about three-eighths of an inch to a little over one inch.

Over the brick bottom is the "lower bench" coal of the bed. This is characteristically a clean coal, but may contain locally some mineral matter and be high in pyrite. It varies in thickness from 32 to 40 inches. (See Plate IV.)

Immediately above the "lower bench" occurs the bone coal, which varies somewhat in texture and from 3 to 13 inches in thickness. This band is known variously as "bone coal," "bony coal," and "bony," but shows no very marked changes in composition. At first glance, it looks like clean coal, but on closer scrutiny proves to be high in mineral matter. In some cases it resembles a

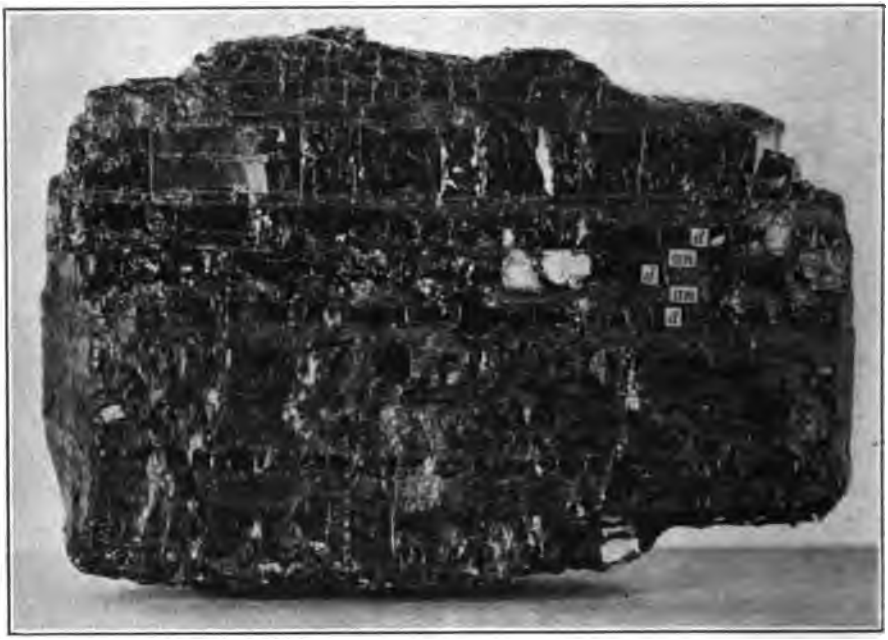


PLATE I.—*Sample of Illinois coal showing laminæ. (d—bands of anthraxylon; an—layers of attritus. Referred to in text as a and b.)*

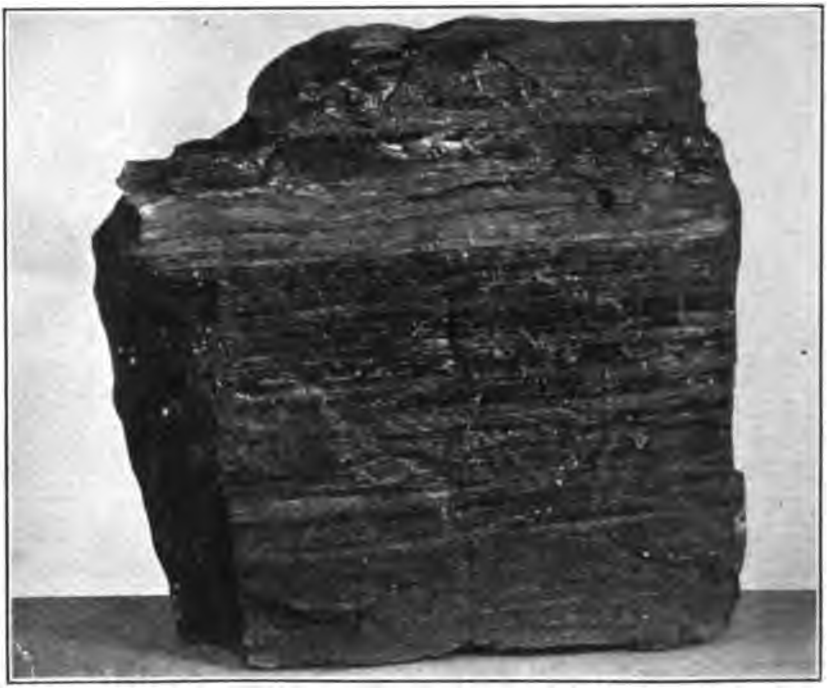


PLATE II.—*Lowest coal or coal above fireclay bottom.*

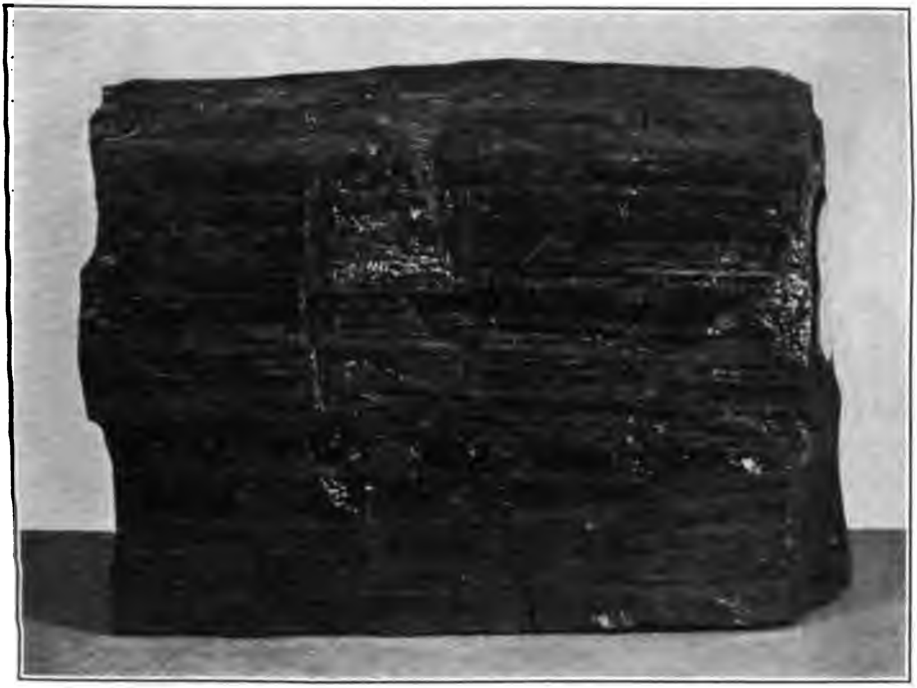


Plate III.—*Second coal or coal below brick bottom.*

Plate IV.—*Lower bench coal.*

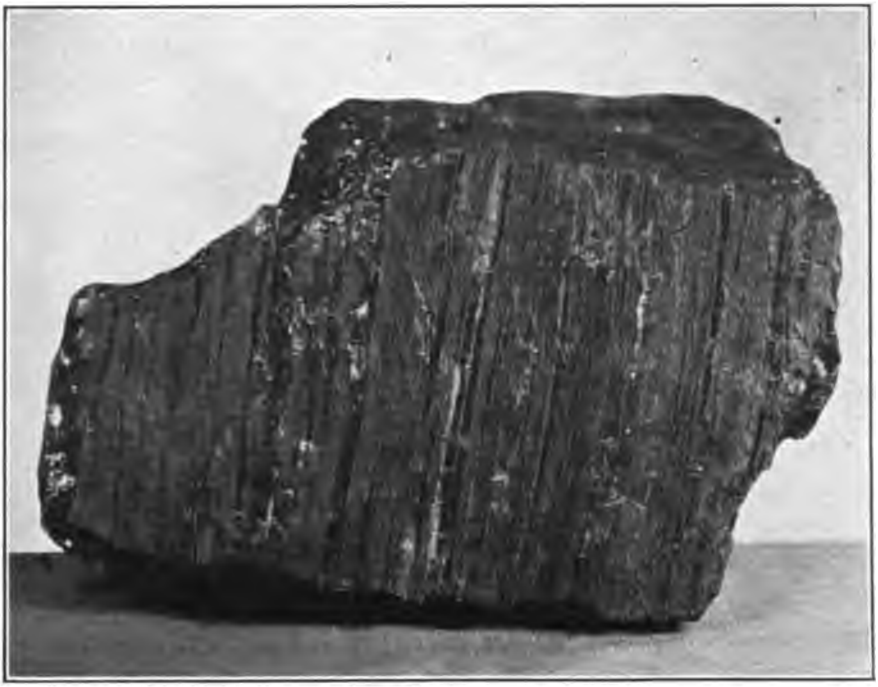


PLATE V.—*Bone coal.*

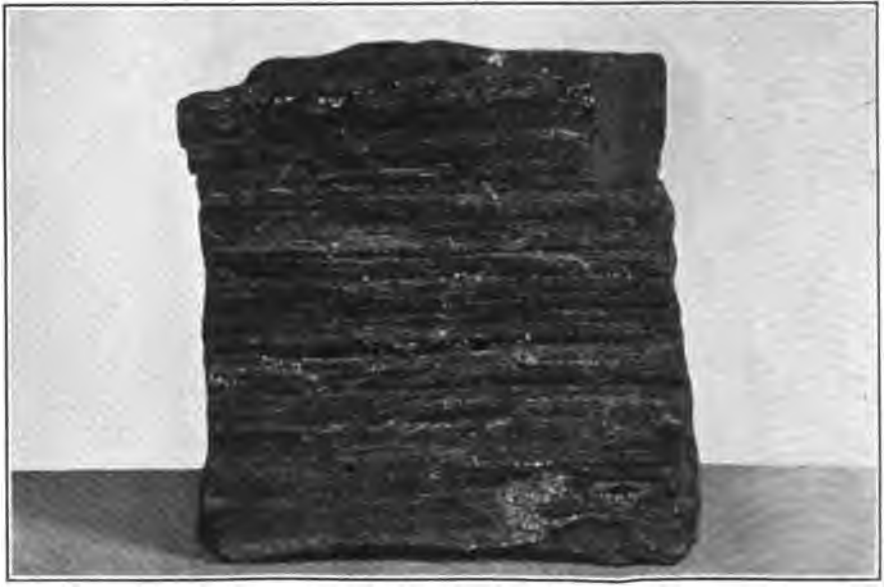


PLATE VI.—*Upper bench coal.*

PLATE VII.—*Cannel coal.*

grey or black shale containing glistening bits of bituminous material. (See Plate V.)

Above the bone coal and below the cannel roof there is a layer of coal called the "upper bench," varying in thickness from 32 to 34 inches, in some localities containing a slate binder of varying thickness, which also varies in its position in the bench. This coal is usually clean, but is very friable in parts of the seam. (See Plate VI.)

At the top of the bed is a layer of cannel coal, and this shows by far the greatest variation in thickness, ranging from a fraction of an inch to 33 inches as a maximum. It is a clean, smooth, grayish-colored cannel, breaking with the typical concoidal fracture, and showing very little pyrite. (See Plate VII.)

Having outlined a columnar section of the seam, it may be well to refer briefly to those portions of the coal which are mined by the companies operating in the areas described. As there is little or no market for the cannel coal, it is usually not removed but is left for a roof, for which purpose it serves very well; although as we shall see later it is too valuable a material to use for roof or to be thrown into the "gob."

The general practice is to mine the upper bench, bone coal, and lower bench, down to the first one-inch shale band, or "brick bottom," and leave the two lower layers of coal in place. This leaves the cannel coal and the two layers below the slate band or "brick bottom" in the worked-out and caved portions of the mine, where they can never be recovered except at great expense. Like the cannel, it is at present not considered of sufficient value to warrant its being mined, but the two thin lower bands contain some of the highest grade coal in the seam.

At present the bone coal is either thrown out onto culm heaps and allowed to weather or burn by spontaneous combustion, or is hauled back in the gob and left for the roof to cave on. It is a great expense to the operators, as it must be handled in order to allow the mining of the lower bench, and at present it yields no returns to pay for its mining and haulage.

MICROSCOPIC INVESTIGATION.

Samples were collected from the five mines mentioned, and included all of the coal from the cannel coal, up to and including layers below the floor or brick bottom, which is usually not mined. Many thin sections were prepared from these samples, and in two instances almost complete series of micro-sections of the seam were made. In other words, microscopic sections of the coal were prepared in sequence from the bottom to the top of the bed, at intervals of not more than an inch or two. This ensured a very representative series of the seam, and gave the same result that would have been obtained by cutting one continuous microsection from top to bottom.

These sections were carefully studied, photomicrographs were taken, and the observed facts correlated with the results of analyses and the products obtained from coking the coal.

In describing the microscopic characteristics of the bed, the most logical method is to start at the bottom of the seam and proceed to the top or cannel coal.

Lowest coal, or that above the fireclay.—The lowest band of coal in the bed is about 5 inches in thickness, but in some cases may thin down to less than 2 inches. (See Plate II.) It exhibits its anthraxylous nature even to the naked eye. In some places the bands of bright coal or anthraxylon are over an inch in thickness.

In microsections this coal appears as almost pure anthraxylon, with very little or no attritus. This anthraxylous character is so marked that some sections look like a series of broad bands of anthraxylon separated by thin layers of somewhat macerated woody matter. (See Plates VIII to X, inclusive.) In many cases, the structure of the wood is very clearly preserved.

Next in quantity to the anthraxylon are the resinous portions which appear as oval homogeneous patches, sometimes scattered throughout the anthraxylon like the resin in wood, and sometimes in clusters where they have been segregated.

There are very few spore-exines present, and these are usually interbedded with cuticles, although in a few local areas the exines of both micro- and mega-spores are scattered sparingly.

In these sections there is a good deal of iron disulphide or pyrite (FeS_2) appearing as small opaque circular or irregular patches. The pyrite can be distinguished from the mother of coal on examination by reflected light, under which the sulphide appears yellow in color while the mineral charcoal remains a dead black.

The binder.—The lowest coal terminates abruptly in a shaly coal called "binder." (See Plate II.) It is a macerated coal very rich in mineral matter with a high sulphur content. The mineral matter decreases in going up, and changes into normal coal, the coal forming the "second layer of coal."

Second layer, or coal below the brick bottom.—The binder, as already noted, changes into normal coal, and forms the next layer of

PLATE VIII.—*Coal six inches below brick bottom. (X200). Resinous anthraxylon with some cuticular matter and scattered masses of pyrite.*

Plate IX.—*Coal five inches below brick bottom. (X200).*

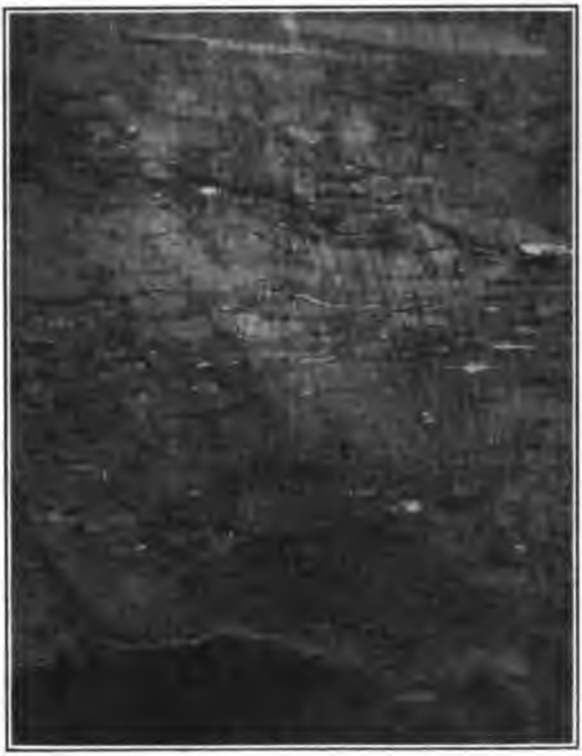


Plate X.—*Coal four inches below brick bottom. (X200). Great concentration of resinous particles.*

coal (see Plates III and XI to XIV) above, from 2 to 4 inches in thickness. Macroscopically it differs from the bottom coal in being composed of bands of anthraxylon, not nearly as thick as in the lowest layer, and also consisting of a larger number of thinner bands. In the coal in contact with the binder the bands are fairly thick, but decrease in thickness going upward. (See Plate III.) The bands are closely packed with but little attritus between them. Microscopically it resembles the bottom band so closely that a separate description is not necessary. The only noticeable difference being that this second layer contains slightly less of the microscopic pyrite and a trifle more of the macerated material.

Brick bottom.—Above the second layer of coal is the shale or brick bottom. This appears as a typical bituminous shale (See Plate XV.), and contains, besides the usual mineral matter, some thin strips of anthraxylon and many highly-carbonized particles.

Lower bench.—The compilation of the lower bench is quite uniform from the bottom to within a few inches of the bone coal. The last few inches indicate disturbances and the coal becomes irregular in its layering. The anthraxylon bands are on the whole relatively thin, ranging from those of microscopic thickness to not more than five millimeters in thickness. (See Plate IV.) The sheets of interbedding attritus are relatively thin. Layers thicker than a few millimeters are rare. Approaching the bone coal the anthraxylon bands increase in thickness and become farther separated by thicker layers of attritus, which becomes rich in mineral matter as the bone coal is approached. Microscopically, in thin sections (See Plates XVI and XXI.) the coal, from the brick bottom to within a few inches from the bone coal, is shown to be anthraxylous. It is compact and quite uniform in texture, with but here and there bands of attritus of appreciable thickness. The larger part of the anthraxylous matter is plainly derived from the woody parts of the plants. Here and there are layers that indicate a derivation of corky parts of plants. In this respect the coal is similar to that of No. 6 Bed of Illinois.

The anthraxylon is fairly rich in resinous matters, particularly in the lower part. The coal of this bench as a whole contains relatively little pyrite in the form of minute granules. The lower part contains more than the upper and in certain sections there is a considerable amount of it.

The attritus is of a humic type—that is, it is chiefly composed of woody degradation matter, together with resinous matters. It is relatively speaking poor in spore matter, chiefly microspores,

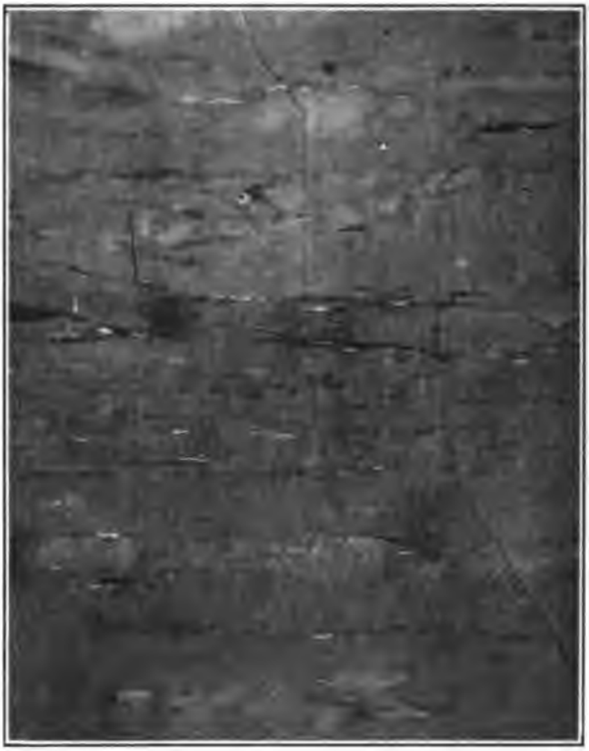


PLATE XI.—*Coal three inches below brick bottom. (X200).*

Plate XII.—*Coal two inches below brick bottom. (X200). Matt of cuticles and few spore-exines.*

Plate XIII.—*Coal one inch below brick bottom. (X200).*

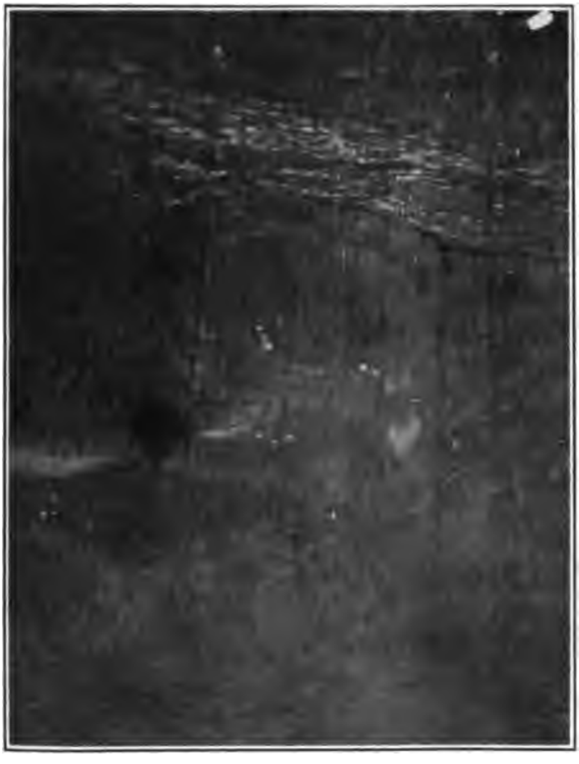


PLATE XIV.—*Immediately below brick bottom. (X200) . Large masses of resinous matter, wavy strips of cuticles, and black spot of pyrite.*

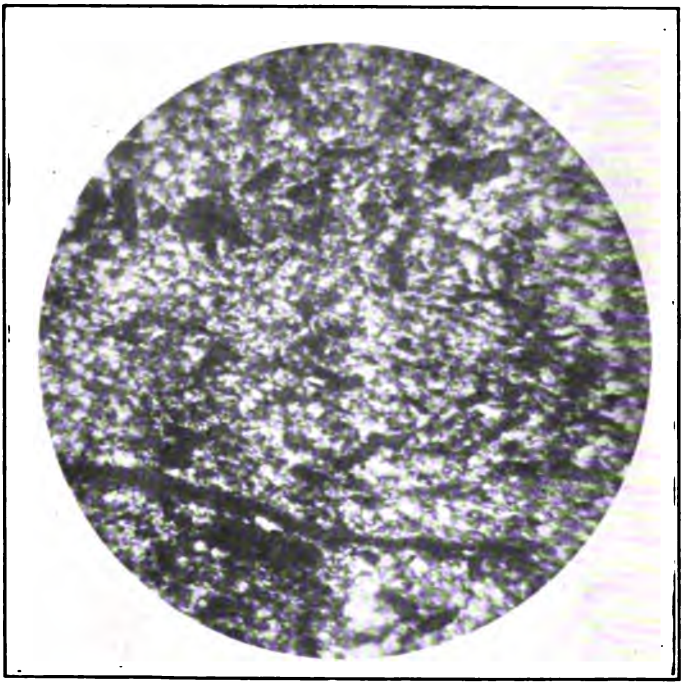


PLATE XV.—*Brick bottom. (X200). Mineral matter, anthraxylon in strips, and irregular patches of mother of coal.*

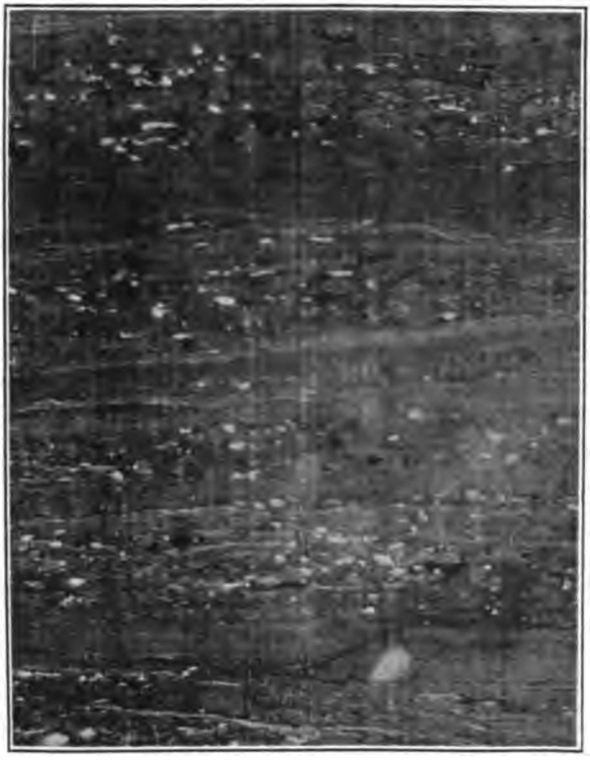


Plate XVI.—*Coal near floor of lower bench. (X200).*

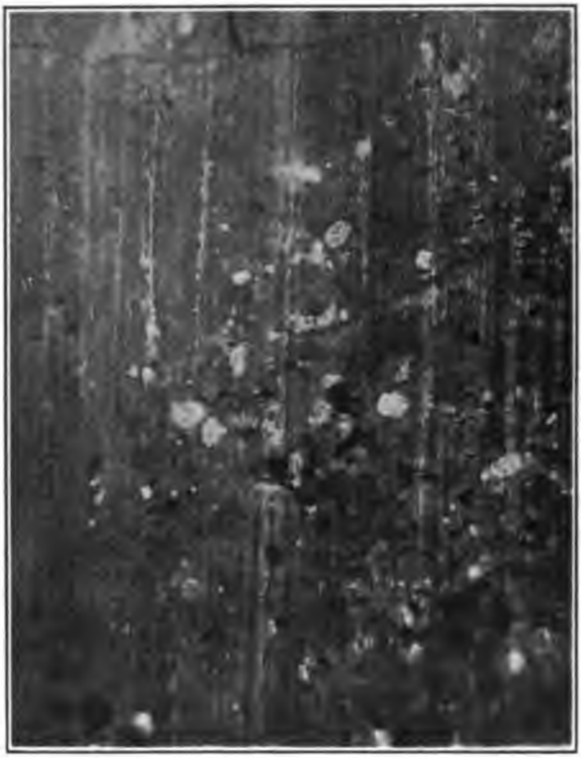


PLATE XVII.—*Horizontal section of coal near floor of lower bench showing characteristic spore-exines. (X200).*

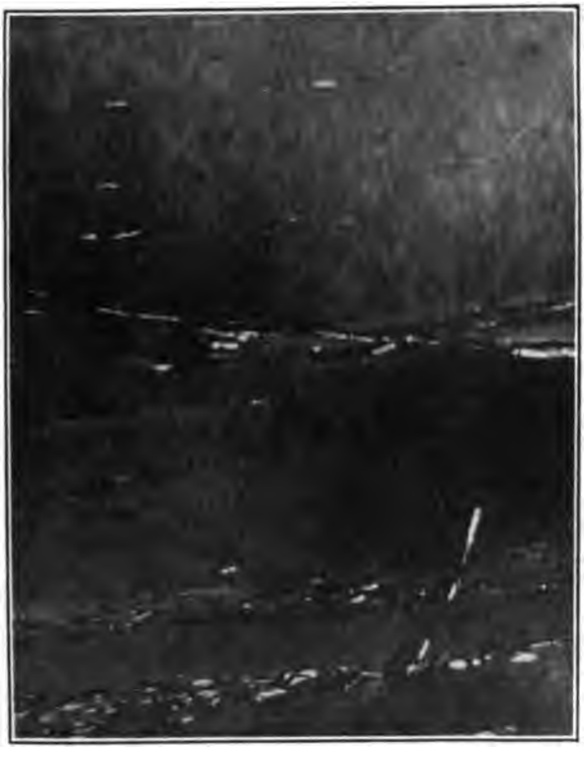


Plate XVIII.—*Coal from lower bench five inches above floor. (X200).*

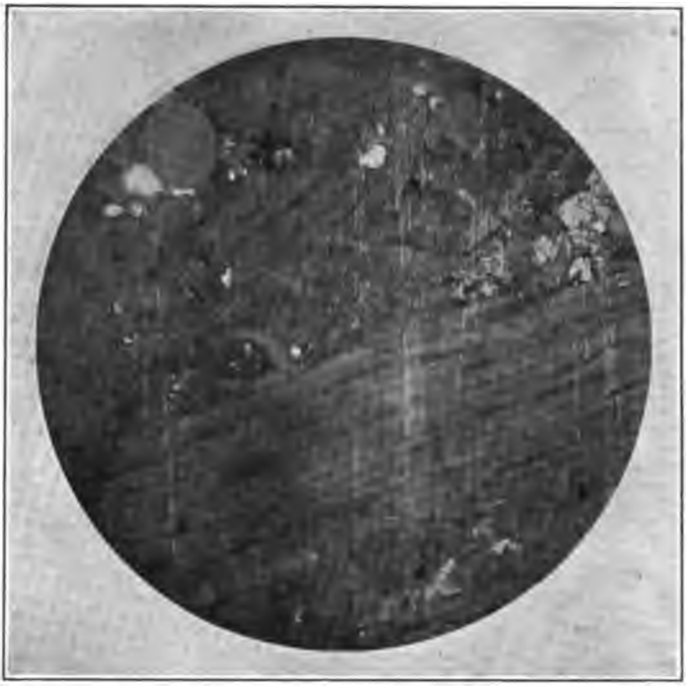


PLATE XIX.—*Horizontal section of lower bench coal five inches above floor. (X200). Woody structure, resinous particles, and few spore-exines.*

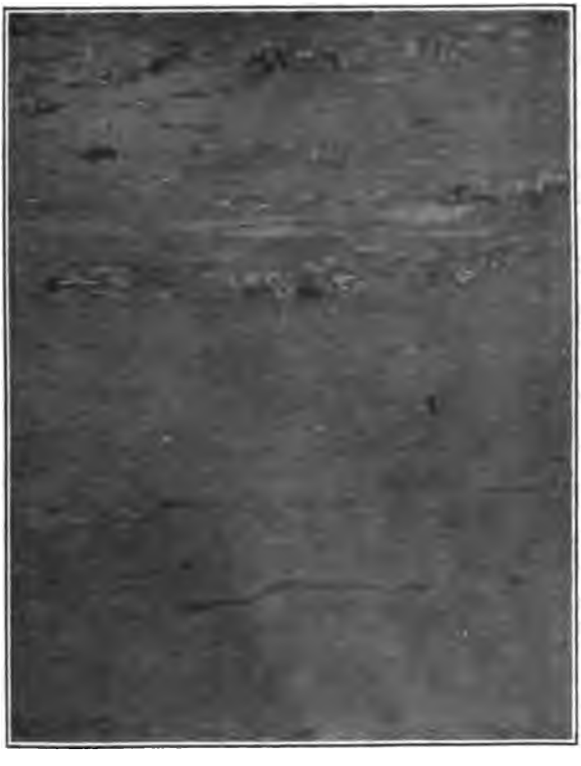


Plate XX.—*Lower bench coal. (X200). Matts of cuticles and exines, with some mother of coal.*

PLATE XXI.—*Horizontal section of lower bench coal. (X200). Woody structure, pyrite, and three of the characteristic spore-exines.*

though some megaspores are present. Cuticles are present in small numbers.

Towards the top the coal is less compact. The anthraxylon bands become thicker and further separated by layers of attritus rich in mineral matter consisting mainly of clay. The anthraxylous matter is of the same nature as that farther down (See Plates XXII to XXV.), but is more opaque and darker in color, becoming more so towards the bone coal.

Bone coal.—The bone coal resembles in outward appearance an ordinary bituminous coal. (See Plate V.) It has all the constituents and characteristics of the other benches in the seam, but intimately mixed with the anthraxylon and attritus is a large amount of finely divided mineral matter, and a somewhat higher content of charcoal.

The question arises whether this mineral matter was a volcanic dust which had been blown into the peat bogs or whether it was ordinary silt washed into it. A petrographic examination of the ash from the bone coal gave no evidence of its being of volcanic origin. It is probably ordinary fine dust which was blown and washed into the bog. The mineral matter consists very largely of kaolin or clayey matter.

The higher content of mother of coal is well shown and is seen to occur in irregular masses, and those opaque patches are rather larger than those which were observed in the other sections of the coal. (See Plates XXVI to XXX.)

The bone coal is a rather peculiar formation, as it is neither a true coal nor a bituminous shale, although it resembles the latter fairly closely. It differs markedly from the oil-shales, as it contains fairly large quantities of anthraxylon and decidedly less spores. Those that are present are both micro- and megaspores, and are of the same type as those found in the remainder of the coal. The anthraxylon is decidedly more opaque in the bone than in the lower bench coal, otherwise of the same nature.

Upper bench.—The bone coal within the space of a few inches decreases in mineral matter and assumes the characteristics of normal coal; and the precise horizon where bone coal ends and coal begins cannot be determined. The amount of mineral matter, which is still chiefly clay, decreases, the anthraxylon strips become lighter in color, and more transparent, and the coal as a whole becomes more compact and homogeneous. (See Plate XXXI.) But soon above the horizon where the coal assumes normalcy it becomes rapidly richer in attritus, and the anthraxylon strips become thinner

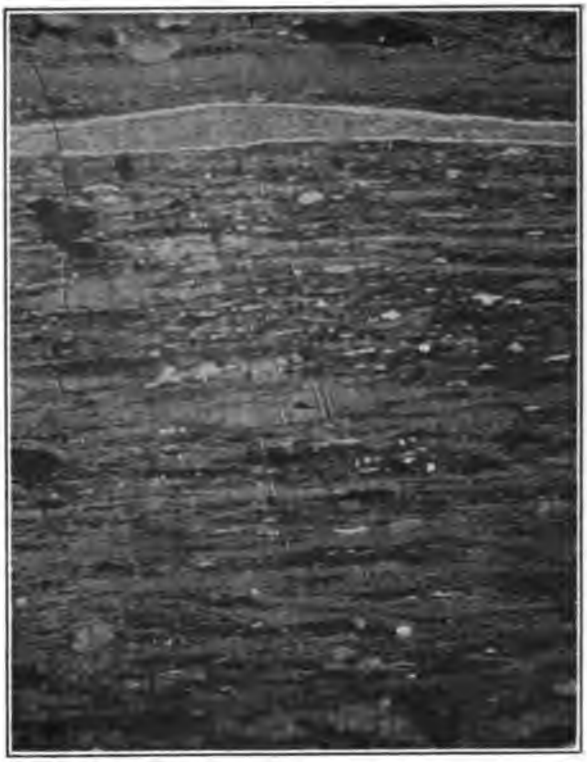


PLATE XXII.—*Lower bench coal. (X200).*

PLATE XXIII.—*Coal just below bone. (X200).*

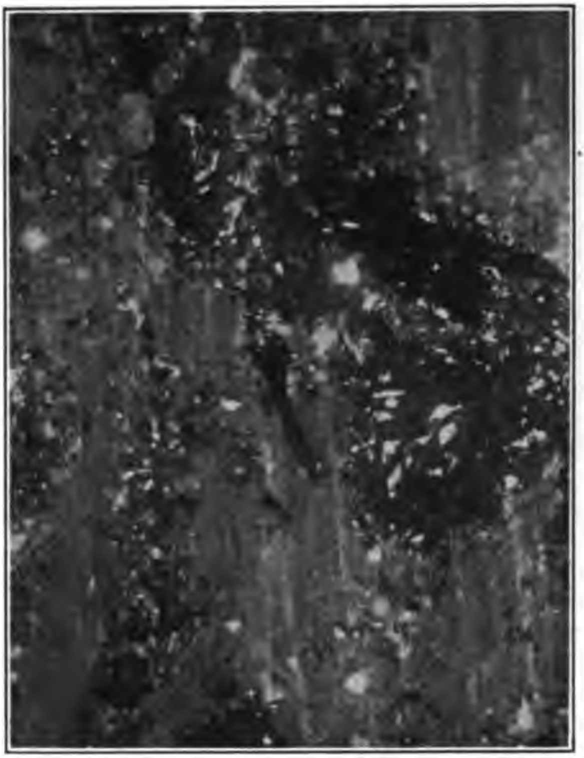


PLATE XXIV.—*Horizontal section of coal just below bone. (X200). Large irregular masses of mother of coal.*

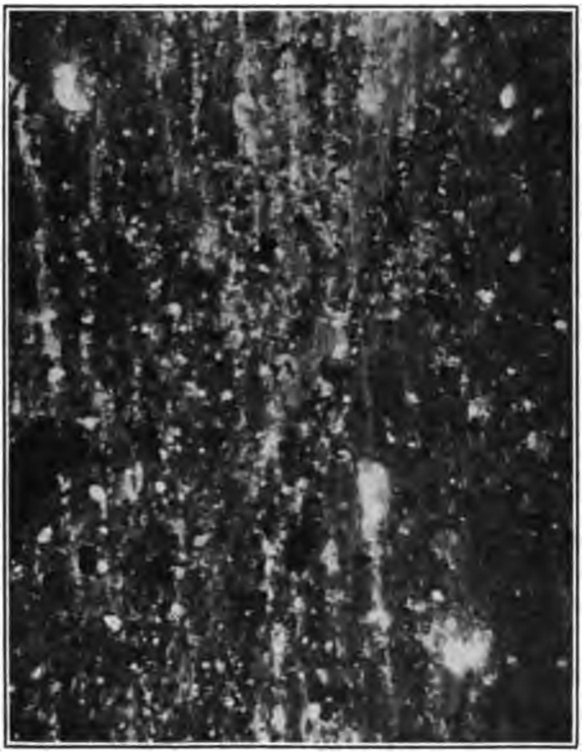


PLATE XXV.—*Horizontal section of coal just below bone. (X200). Mineral matter, spore-exines, and mother of coal.*

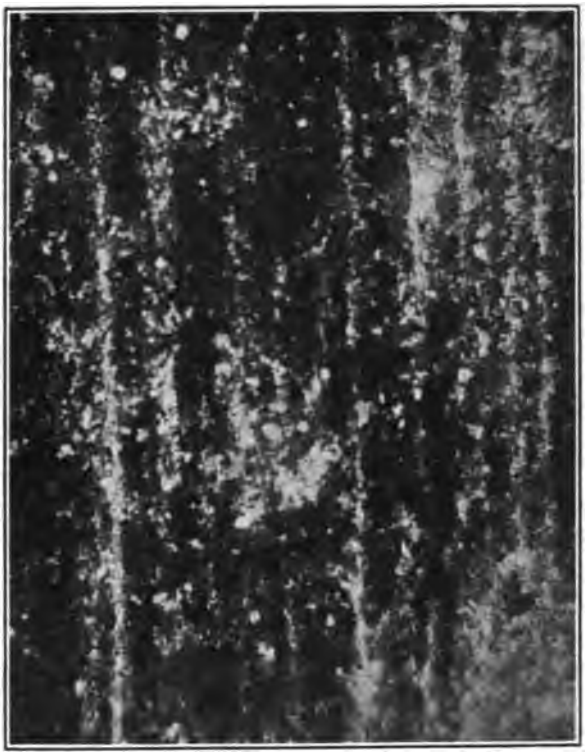


Plate XXVI.—*Bone coal showing mineral matter. (X200).*

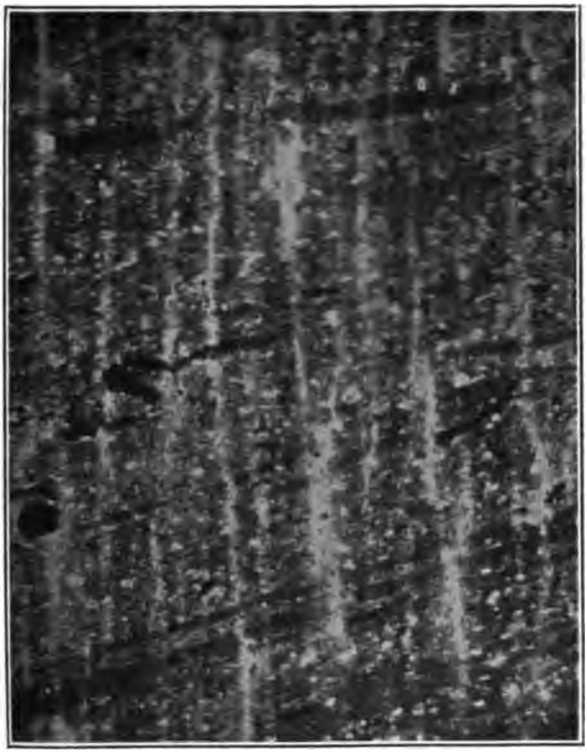


PLATE XXVII.—*Bone coal. (X200).*

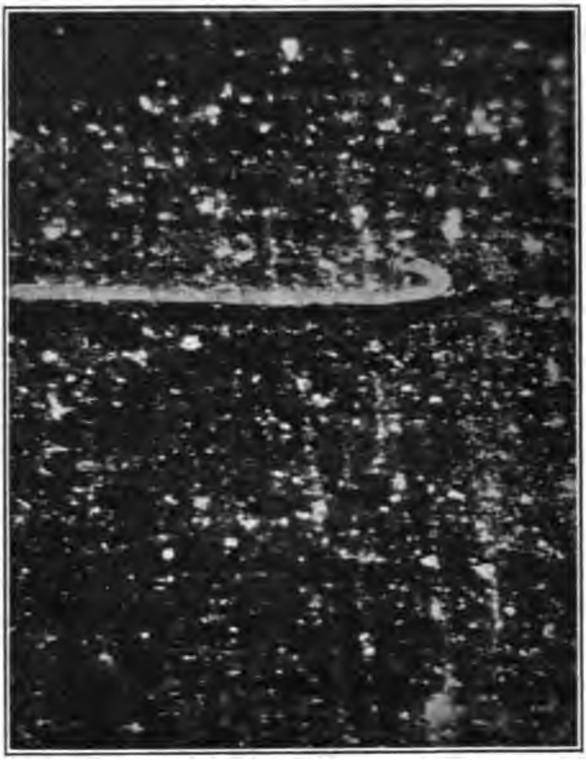


Plate XXVIII.—*Bone coal. (X200). Large platter-shaped spore-exine.*

PLATE XXIX.—*Horizontal section of bone coal. (X200).*

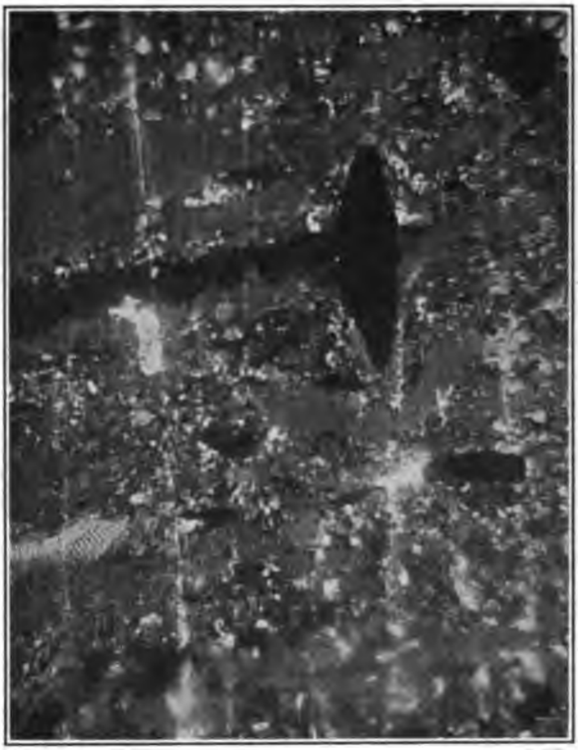


PLATE XXX.—*Horizontal section of bone coal. (X200). Well-preserved traechea at near left bottom corner.*

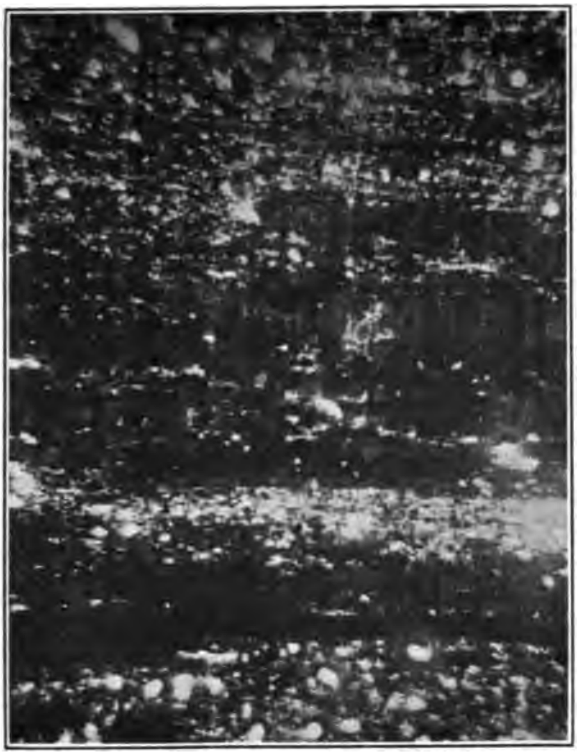


PLATE XXXI.—*Coal just above bone. (X200).*

and lie farther apart. The coal is now attritious, containing a considerable amount of anthraxylous matter. (See Plate XXXII.) But in proceeding upward (See Plates XXXIII to XXXV.) the latter gradually decreases until within a short distance from the cannel coal it is almost all attritus. (See Plates XXXVI to XXXIX.)

Within a few inches below the overlying cannel coal the anthraxylon strips become irregular, change to irregular fragments, and just below the cannel the anthraxylon no longer occurs as strips but only as irregular, coarse, granular, degradation matter embedded together with spores in a finer dark-colored degradation matter, the whole resembling a shale. (See Plates XL and XLI.)

The upper bench is considerably richer both in spore and in resinous matter than the lower bench and increasingly from the bottom up. Besides the spores a considerable amount of cuticular matter is scattered throughout the coal of the upper bench.

The attritus is of a fine granular matter consisting chiefly of woody degradation matter in a granular state. Resinous matter is also a prominent constituent. Spores and cuticular matters form the lesser part.

Cannel coal.—As already shown, the upper bench coal rapidly changes from a laminated coal into a coarse granular attritus. This is but the transition from laminated coal into unlaminated coal and marks the transition line between coal and cannel coal.

The coarse granular structure rapidly changes into a much finer granular structure and now contains a much larger number of spore matter. At this time the coal assumes the unlaminated smooth structure with a concoidal fracture—the cannel structure. (See Plates XLII and XLIII.)

The cannel coal is composed of woody degradation and other humic matter, spore matter, resinous matter, cuticular matter and few more highly carbonized particles all embedded in a very finely macerated dark and opaque ground mass. The humic matter forms the chief constituent, and the spore matter is the next important.

This cannel coal may be defined as a humic-spore coal. Only in a few horizons is there more spore matter than humic matter.

It may be noted at this point that the cannel coals of Western Pennsylvania may be classified into three classes: Spore coals, humic coals and boghead coals. The cannel coal at Cannelton, Pa. is a typical spore cannel coal and is very largely composed of spore-matter. A cannel coal near Nealy's Station in Butler County, Pennsylvania is a typical humic cannel coal. By far the largest part of formed by humic degradation matter. A cannel coal near Kiskiminetas Junction in Westmoreland County, Pennsylvania, lying between the upper and the lower Freeport coal beds, is a typical boghead coal. A coal is never composed of one constituent alone but other constituents, such as are usually present, are always mixed in with the main one. At times one or more constituents may occur in more or less appreciable amounts and lend the characteristic nature to the bed. In the thick Freeport cannel coal, humic matter forms the main constituent and spore matter the next, and so may be designated as a humic-spore cannel coal.

The lower half of the cannel coal is relatively low in ash, while the upper part is very high in ash. In going upward there is a gradual increase in mineral constituents which increases rapidly above the middle of the layer, so that it grades into a bituminous shale on top and finally ends in a shale altogether.

The thick Freeport bed as a whole is to be considered as one bed, and not as a compilation of several beds deposited at different separate periods. The various bands and layers were the results of minor disturbances that came during the period and again disappeared, leaving none or slight changes in the deposit as a whole after the disturbances had ceased. Thus certain disturbances caused layers of clay to be deposited, giving rise to shale bands or bony coal. On one occasion this disturbance appears to have been quite protracted, giving rise to the layer of bone coal. But when the disturbances were over the coal assumed its normal condition.

During the whole time of the deposition of the bed, there occurred, however, far-reaching and permanent disturbances which brought about changes in the character of the coal as a whole. The bed began with a woody swamp under mesopthytic to hydrophytic conditions. This gave rise to a woody or anthraxylous coal. The condition then relatively rapidly changed into a more hydrophytic and a less anthraxylous and a more attritious coal was the result, such as is found in the lower bench coal. For a long time there was only a slight change, causing but a slight change in the coal until the time when the disturbance causing the bone coal came. Soon after the disturbance that caused the bone coal to be laid down, there was a more rapid change in to more hydrophytic conditions and increasingly so continuing throughout the deposition of the upper bench coal. The result was a highly attritious coal. Suddenly the conditions must have become almost aquatic and the result was the cannel coal.

The coal begins with the inclusion of two types of predominant spores. One of these is characteristically sculptured and is shown in Plate XLIV: the other is a smooth-walled spore discern-

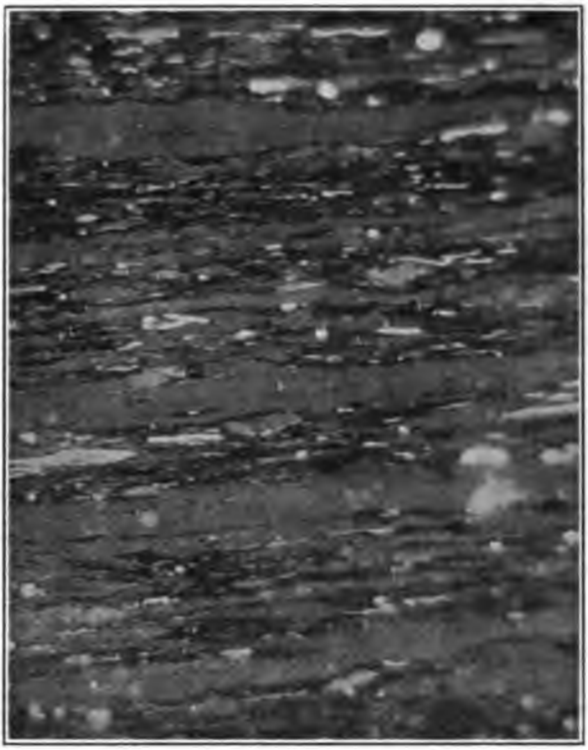


PLATE XXXII.—*Coal above bone. (X200).*

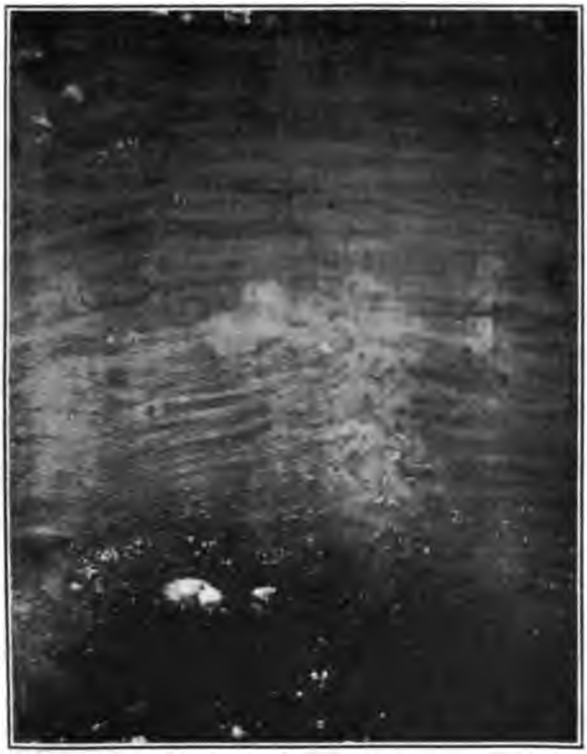


PLATE XXXIII.—*Horizontal section of coal 19 inches below roof plainly showing woody structure. (X200).*

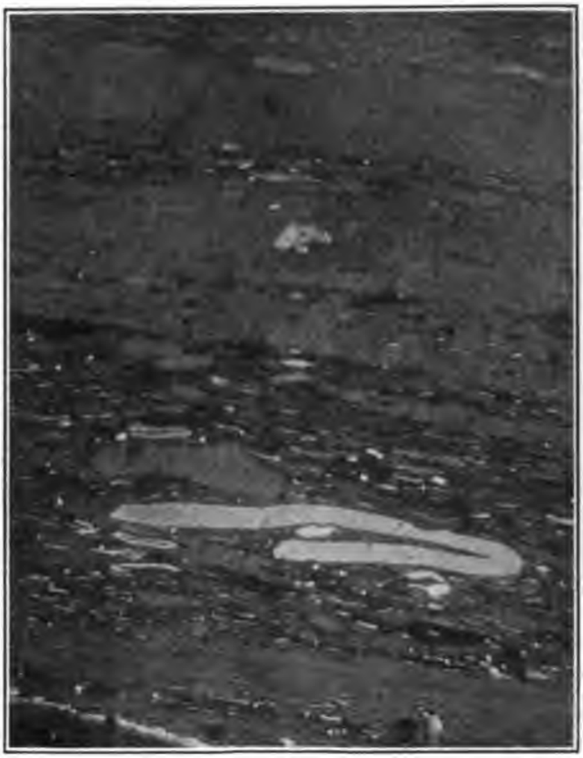


PLATE XXXIV.—*Coal 25 inches below roof. (X200).*

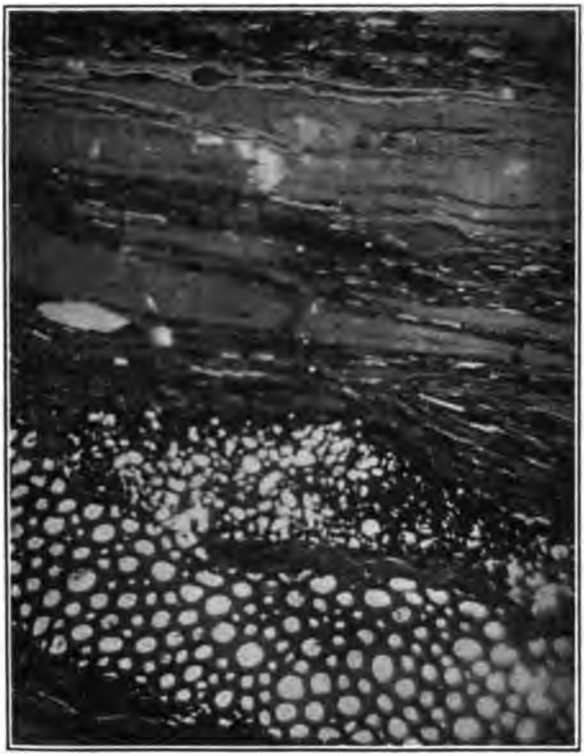


PLATE XXXV.—*Coal 10 inches below roof showing group of nut-cells and woody structure. (X200).*

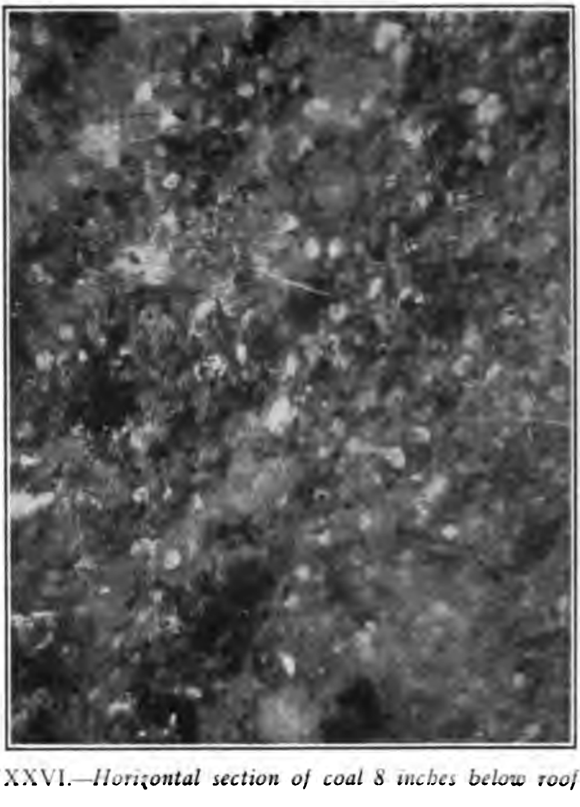
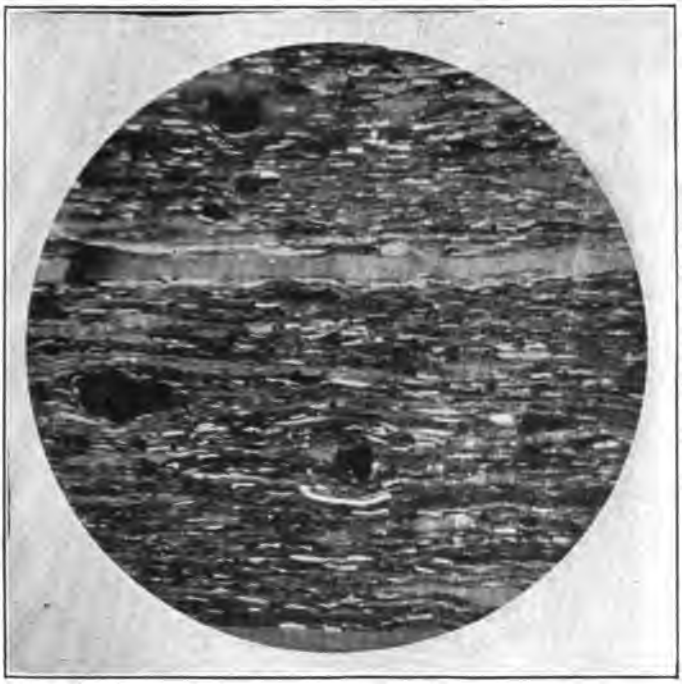
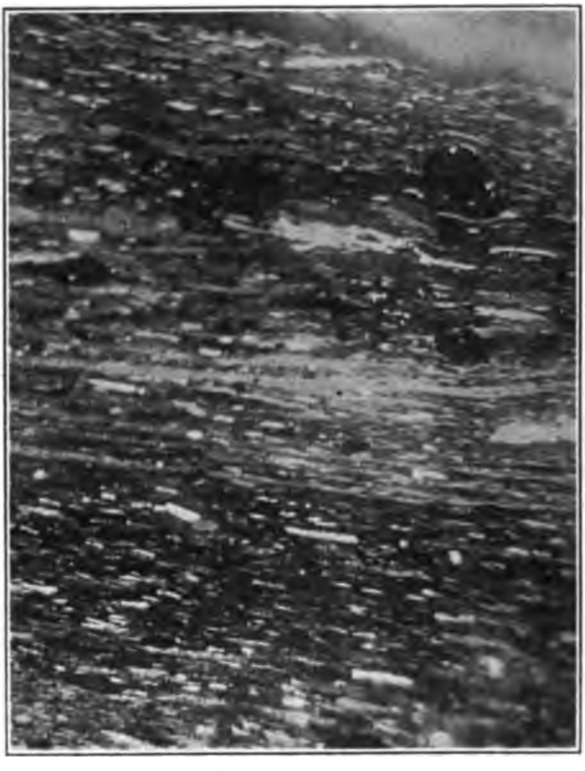


Plate XXXVI.—*Horizontal section of coal 8 inches below roof. (X200).*



PATE XXXVII.—*Coal 8 inches below roof. (X200).*



PATE XXXVIII.—*Coal 8 inches below roof. (X200).*

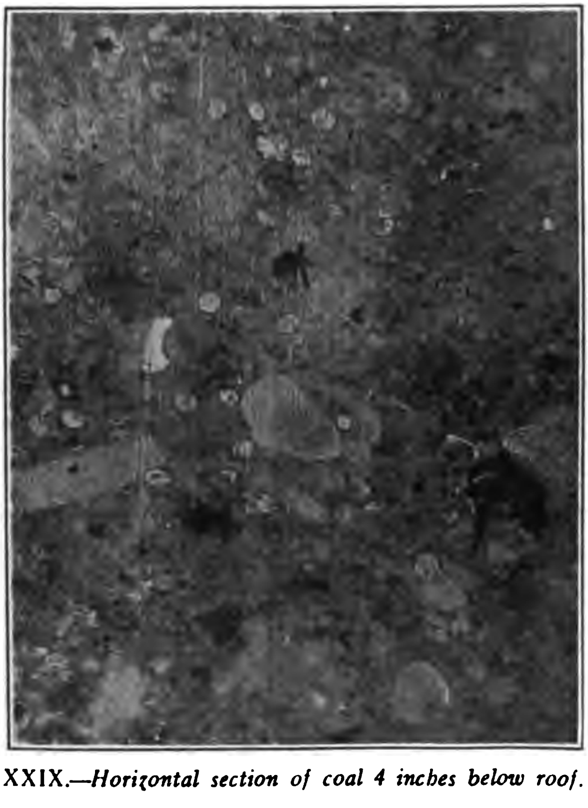


Plate XXXIX.—*Horizontal section of coal 4 inches below roof. (X200).*

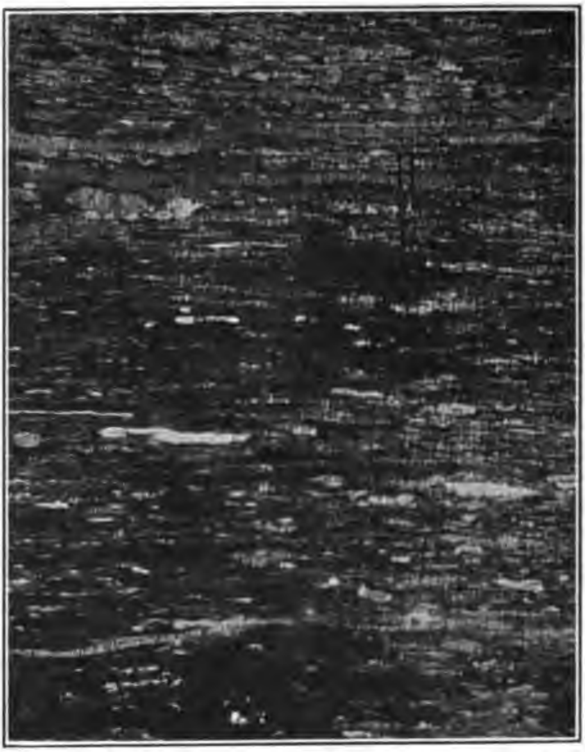


PLATE XL.—*Coal 4 inches below roof. (X200).*

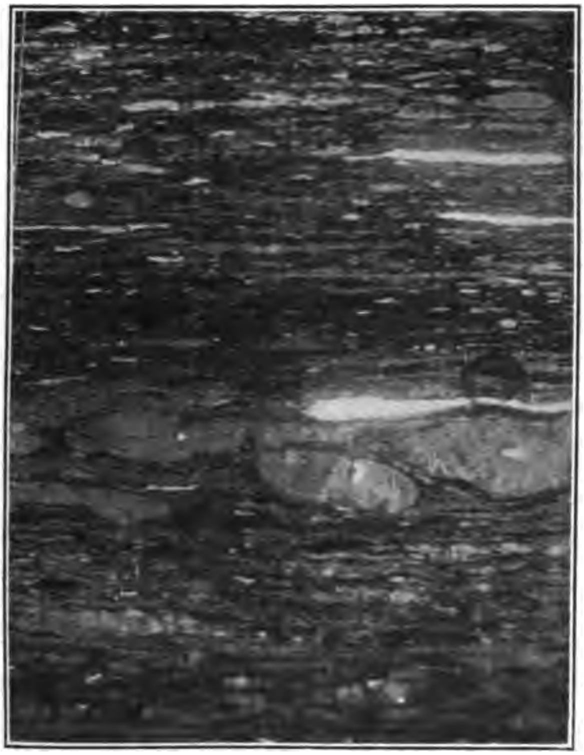


Plate XLI.—*Coal 4 inches below roof. (X200).*

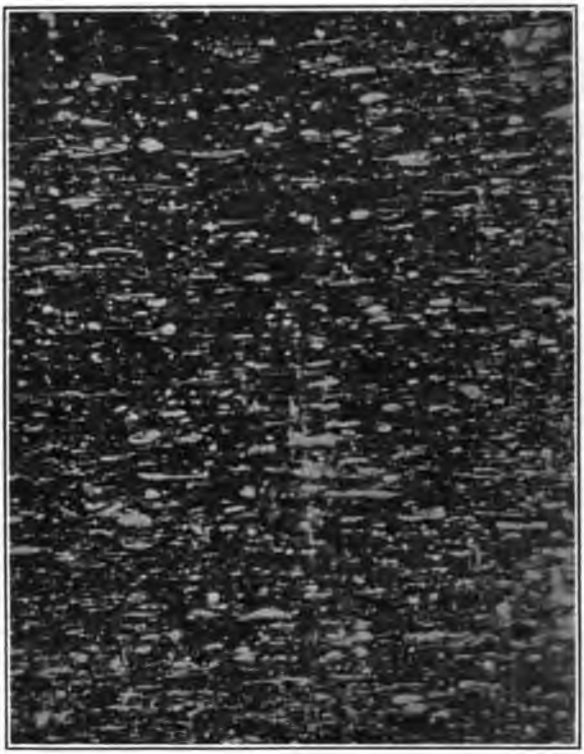


PLATE XLII.—*Cannel coal near top. (X200).*

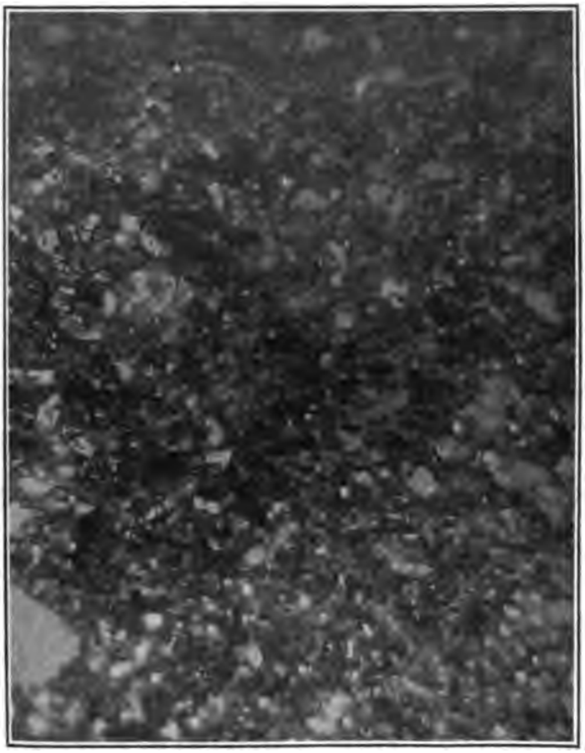


Plate XLIII.—*Horizontal section of cannel coal. (X200).*

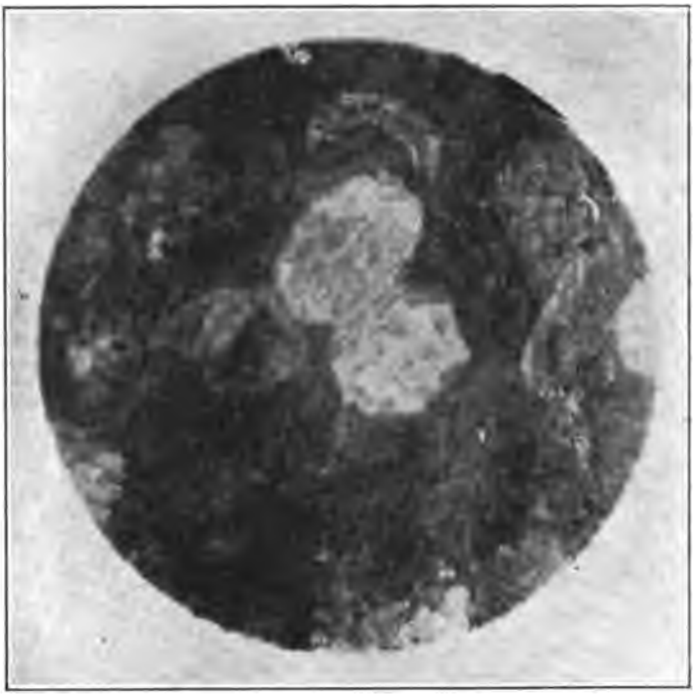


PLATE XLIV.—*Typical spore-exines from Freeport seam from New Field mine. (X1000).*

able in almost all the photographs. The latter is prominent throughout the bed from bottom to top. The former, a rough coated spore, is very prominent in the lower layers and in the lower part of the lower bench, but decreases in numbers proceeding upward and a few inches below the bone coal is but sparingly present, and continues thus to the top of the seam. About two-thirds up in the lower bench coal a very peculiar, very thick-walled spore appears, in but relatively small numbers, and persists throughout the rest of the bed upward, including the bone coal and the cannel coal.

The persistence of these spores, as well as other characteristics throughout the bed, would indicate that the bone coal is not a partition marking the approach and coalescence of two separate coal beds.

CORRELATION.

It seemed reasonable to suppose that anthraxylon, attritus, and mother of coal would behave differently on coking, owing to the very different materials which entered into their composition, so it was decided to see how each would act when subjected to dry distillation.

About five grams of each of the constituents were carefully picked out by hand. This work was accomplished by means of a strong knife and a pair of forceps. Each tiny bit of coal was examined under a magnifying glass to be sure that it was as nearly a pure constituent as possible.

The actual coking was done in a small electric furnace, where the pyrex tubes containing the hand-picked samples could be heated slowly, and the temperature carefully observed and controlled.

After slowly raising the temperature to 600° C., it was held constant for half an hour, when the current was cut off, and the furnace, pyrex tubes and coke were allowed to cool to room temperature. After this the residue from each constituent was examined and the differences noted.

It was found that the anthraxylon yielded a very metallic mass, which appeared to have been completely fused. It contained many cell-spaces which were not connecting, and were of rather large size.

The attritus yielded a much less metallic mass with smaller but more numerous pore-spaces which appeared to be somewhat interconnected. This mass showed signs of much less complete fusion, was much more friable, and lacked the marked metallic ring of the residue from the anthraxylon.

The mother of coal remained in the form of a dry, black, unfused powder, and appeared to have been practically unchanged by the heating.

In these tests, which were of a very preliminary character, the distillates were entirely neglected, as the quantity was insufficient to permit of their being studied and also because this work was being carried out by J. D. Davis and H. G. Berger (See Bulletin 1, Carnegie Institute of Technology.) and only the solid residues were examined.

These preliminary tests indicated clearly that anthraxylon and attritus differ in their chemical as well as their physical properties, so that it was thought worth while to carry on some more exact tests on a larger scale. For these tests, the constituents were hand-picked from a sample of Illinois coal, because in that coal the laminæ of anthraxylon and attritus were wider and more clearly differentiated than in the Pennsylvanian coals. About two pounds of as nearly pure anthraxylon and attritus as was possible to select were hand-segregated, and a sample of each was analyzed by the standard method of the Bureau of Mines. (See tables 1 and 2.)

TABLE 1.—*Analysis of hand-segregated anthraxylon from Illinois coal.*

Proximate analysis.

	Coal. (Air dried)	Coal. (As received)	Coal. (Moisture free)	Coal. (Moisture and ash free)
Moisture	5.9	5.9	.....	.....
Volatile matter	33.4	33.4	35.5	36.9
Fixed carbon	57.2	57.2	60.8	63.1
Ash	3.5	3.5	3.7	.....
	100.0	100.0	100.0	100.0

Ultimate analysis.

	Coal. (Air dried)	Coal. (As received)	Coal. (Moisture free)	Coal. (Moisture and ash free)
Hydrogen	5.3	5.3	4.9	5.1
Carbon	74.0	74.0	78.6	81.6
Nitrogen	1.4	1.4	1.5	1.5
Oxygen	14.8	14.8	10.2	10.7
Sulphur	1.0	1.0	1.1	1.1
Ash	3.5	3.5	3.7	.....
	100.0	100.0	100.0	100.0

Calorific value.

	Coal. (Air dried)	Coal. (As received)	Coal. (Moisture free)	Coal. (Moisture and ash free)
Calories	7217	7217	7665	7961
B. t. u.	12990	12990	13800	14330

TABLE 2.—*Analysis of band-segregated attritus from Illinois coal.*

Proximate analysis.

	Coal. (Air dried)	Coal. (As received)	Coal. (Moisture free)	Coal. (Moisture and ash free)
Moisture	3.0	3.0	.....	.....
Volatile matter	34.3	34.3	35.3	39.6
Fixed carbon	52.2	52.2	53.8	60.4
Ash	10.5	10.5	10.9	.....
	100.0	100.0	100.0	100.0

Ultimate analysis.

	Coal. (Air dried)	Coal. (As received)	Coal. (Moisture free)	Coal. (Moisture and ash free)
Hydrogen	4.9	4.9	4.7	5.3
Carbon	70.1	70.1	72.3	81.1
Nitrogen	1.3	1.3	1.4	1.5
Oxygen	12.0	12.0	9.4	10.7
Sulphur	1.2	1.2	1.3	1.4
Ash	10.5	10.5	10.9	.....
	100.0	100.0	100.0	100.0

Calorific value.

	Coal. (Air dried)	Coal. (As received)	Coal. (Moisture free)	Coal. (Moisture and ash free)
Calories	6883	6883	7096	7960
B. t. u.	12390	12390	12770	14330

The analysis seemed to indicate that a difference in by-products was to be expected, so that the two-pound samples were coked in a small vacuum retort and the yields analyzed. The results of this test bore out the predictions made from the microscopic examination, and are included in an unpublished paper by H. G. Berger[15] and the junior author.

CONCLUSIONS.

After careful megascopic, microscopic, and chemical study of the coal, and a correlation of the results of the various phases of the problem, the most striking information obtained is the fact that there is a marked variation in the structure of the Freeport coal from the bottom to the top of the bed, and that the individual benches also vary in composition from bottom to top. At the top of the upper bench is found a coal composed almost entirely of spore-exine-rich attritus, and containing much humic but very little anthraxylon. This concentration of spore and pollen exines, cuticles, and humic matter is so pronounced that in some of the sections this portion of the coal resembles a cannel, and differs from one chiefly in its much more pronounced bedding.

---

[15] Berger, H. G., research fellow at Carnegie Institute of Technology and the Pittsburgh Experiment Station of the U. S. Bureau of Mines.

This composition changes gradually as the bottom of the bench is approached, until the coal nearest the bottom is found to be of an extremely anthraxylous or woody character. In the sections from this portion of the bench, the wide layers of anthraxylon interbedded with thin patches of woody attritus and resinous matter are very conspicuous. This gradation will be readily seen from the series of photomicrographs illustrated by the plates accompanying this paper.

In the lower bench, this same variation was found, but to a less marked degree. In this bench, although the variation was very marked, it was also clearly seen that the whole bench was more anthraxylous than the upper bench.

This same variation was observed in the cannel, and to a less marked degree in the bone coal.

The variation from attritus-rich near the top to an anthraxylous-rich near the bottom of the bed is persistent throughout the area examined, and is not a peculiarity of one mine. This variation in the microstructure is also shown by the analysis of different parts of the seam, and by the coke and distillation products obtained from each portion.

The bone coal is similar in constitution to the coal from the remainder of the seam, and shows the same variation from attritus-rich to anthraxylous-rich portions. The bone coal is different however, from the remainder of the coal in its exceedingly high mineral content; but even with this, it compares favorably with the best grades of bituminous coal mined in some countries.

Below are given the results of an analysis of the Freeport bone coal and from a sample of Brazilian coal.

Proximate analysis—per cent.

	Brazilian coal. (Air dried)	Bone coal—New Field mine. (Air dried)
Moisture	**2.50**	**0.70**
Volatile matter	**29.40**	**25.40**
Fixed carbon	**35.95**	**36.62**
Ash	**32.15**	**37.28**
Sulphur	**0.69**	**0.98**
B. t. u.	**8684**	**9064**

From these figures and from the yields of by-products obtained from this bone coal it is evident that it would be of great value in some countries, although in Pennsylvania it is thrown away. It is further evident that as high-grade coal becomes scarcer, this bone coal will become a marketable product in the United States.

As oil becomes scarce, and more and more benzol is used, the cannel coal, which is now not mined, will be valuable, as upon distillation the yields from the cannel compares with the yields obtained from oil-shale.

As a result of this investigation, it appears that it will be only a matter of time before the entire Freeport seam will be mined from top to fireclay bottom, and the various portions used to greater advantage.

Tables 3 to 7, inclusive, give the analyses of cannel, upper bench and lower bench coals, and coals below the floor and slate.

TABLE 3.—*Analysis of cannel coal from roof of Creighton mine.*

Proximate analysis.

	Coal. (Air dried)	Coal. (As received)	Coal. (Moisture free)	Coal. (Moisture and ash free)
Moisture	0.28	0.49	......	......
Volatile matter	30.77	30.71	30.86	43.35
Fixed carbon	40.22	40.13	40.33	56.65
Ash	28.73	28.67	28.81	......
	100.00	100.00	100.00	100.00

Ultimate analysis.

	Coal. (Air dried)	Coal. (As received)	Coal. (Moisture free)	Coal. (Moisture and ash free)
Hydrogen	4.44	4.45	4.42	6.21
Carbon	60.57	60.44	60.74	85.32
Nitrogen	1.19	1.19	1.20	1.69
Oxygen	4.30	4.48	4.06	5.70
Sulphur	0.77	0.77	0.77	1.08
Ash	28.73	28.67	28.81	......
	100.00	100.00	100.00	100.00

Calorific value.

	Coal. (Air dried)	Coal. (As received)	Coal. (Moisture free)	Coal. (Moisture and ash free)
Calories	6112	6099	6129	8609
B. t. u.	11002	10979	11033	15498

TABLE 4.—*Analysis of upper bench, Freeport seam, Creighton mine.*

Proximate analysis.

	Coal. (Air dried)	Coal. (As received)	Coal. (Moisture free)	Coal. (Moisture and ash free)
Moisture	1.0	2.2	.....	.....
Volatile matter	36.9	36.5	37.3	39.6
Fixed carbon	56.4	55.6	56.9	60.4
Ash	5.7	5.7	5.8	.....
	100.0	100.0	100.0	100.0

Ultimate analysis.

	Coal. (Air dried)	Coal. (As received)	Coal. (Moisture free)	Coal. (Moisture and ash free)
Hydrogen	5.3	5.4	5.2	5.6
Carbon	78.1	77.2	78.9	83.7
Nitrogen	1.7	1.7	1.7	1.8
Oxygen	7.5	8.3	6.7	7.1
Sulphur	1.7	1.7	1.7	1.8
Ash	5.7	5.7	5.8	.....
	100.0	100.0	100.0	100.0

Calorific value.

	Coal. (Air dried)	Coal. (As received)	Coal. (Moisture free)	Coal. (Moisture and ash free)
Calories	7811	7717	7889	8372
B. t. u.	14060	13890	14200	15070

TABLE 5.—*Analysis of lower bench, Freeport seam, Creighton mine.*

Proximate analysis.

	Coal. (Air dried)	Coal. (As received)	Coal. (Moisture free)	Coal. (Moisture and ash free)
Moisture	1.3	1.6	.....	.....
Volatile matter	35.4	35.2	35.8	39.1
Fixed carbon	55.0	54.9	55.8	60.9
Ash	8.3	8.3	8.4	.....
	100.0	100.0	100.0	100.0

Ultimate analysis.

	Coal. (Air dried)	Coal. (As received)	Coal. (Moisture free)	Coal. (Moisture and ash free)
Hydrogen	5.2	5.2	5.2	5.6
Carbon	75.9	75.7	76.9	83.9
Nitrogen	1.6	1.5	1.6	1.7
Oxygen	6.9	7.2	5.8	6.5
Sulphur	2.1	2.1	2.1	2.3
Ash	8.3	8.3	8.4	.....
	100.0	100.0	100.0	100.0

Calorific value.

	Coal. (Air dried)	Coal. (As received)	Coal. (Moisture free)	Coal. (Moisture and ash free)
Calories	7567	7544	7667	8367
B. t. u.	13620	13580	13800	15060

TABLE 6.—*Analysis of coal No. 1 below floor, Creighton mine.*

Proximate analysis.

	Coal. (Air dried)	Coal. (As received)	Coal. (Moisture free)	Coal. (Moisture and ash free)
Moisture	.25	.99	......	......
Volatile matter	38.87	38.59	38.98	42.61
Fixed carbon	52.35	51.98	52.50	57.39
Ash	8.50	8.44	8.52	......
	100.00	100.00	100.00	100.00

Ultimate analysis.

	Coal. (Air dried)	Coal. (As received)	Coal. (Moisture free)	Coal. (Moisture and ash free)
Hydrogen	5.13	5.17	5.11	5.59
Carbon	74.64	74.11	74.85	81.82
Nitrogen	1.50	1.49	1.50	1.64
Oxygen	5.82	6.41	5.60	6.12
Sulphur	4.41	4.38	4.42	4.83
Ash	8.50	8.44	8.52	......
	100.00	100.00	100.00	100.00

Calorific value.

	Coal. (Air dried)	Coal. (As received)	Coal. (Moisture free)	Coal. (Moisture and ash free)
Calories	7609	7555	7631	8342
B. t. u.	13697	13600	13736	15015

TABLE 7.—*Analysis of coal below slate, Freeport seam, Creighton mine.*

Proximate analysis.

	Coal. (Air dried)	Coal. (As received)	Coal. (Moisture free)	Coal. (Moisture and ash free)
Moisture	1.2	2.8	.....	.....
Volatile matter	32.2	31.9	32.6	37.6
Fixed carbon	53.5	52.9	54.2	62.4
Ash	13.1	12.9	13.2	.....
	100.0	100.0	100.0	100.0

Ultimate analysis.

	Coal. (Air dried)	Coal. (As received)	Coal. (Moisture free)	Coal. (Moisture and ash free)
Hydrogen	5.0	5.0	4.9	5.6
Carbon	72.1	71.3	73.0	84.1
Nitrogen	1.4	1.4	1.4	1.7
Oxygen	7.3	8.8	6.4	7.3
Sulphur	1.1	1.1	1.1	1.3
Ash	13.1	12.9	13.2	.....
	100.0	100.0	100.0	100.0

Calorific value.

	Coal. (Air dried)	Coal. (As received)	Coal. (Moisture free)	Coal. (Moisture and ash free)
Calories	7150	7072	7233	8339
B. t. u.	12870	12730	13020	15010

Certain spore-exines which are characteristic of the Freeport bed, namely the micro-spore exines, with a peculiar rough or short-horned surface (See Plate XLIV.) and a more or less pear-shaped, smooth-walled exine persist throughout the bed. Another characteristic spore-exine appears above the middle of the lower bench and persists throughout the rest of the bed upward.

A brief summary of the conclusions reached is as follows:

1. The Freeport bed varies in composition vertically but not horizontally.

2. The different benches also show a variation from top to bottom.

3. Many valuable products can be obtained by the distillation of the bone and cannel constituents, and these are higher grade fuels than the literature would lead one to suppose.

4. The various constituents have different coking properties and by-products.

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CRAFTON, PA.

Bulletin 3

COAL-MINING INVESTIGATIONS

UNDER AUSPICES OF

CARNEGIE INSTITUTE OF TECHNOLOGY,
UNITED STATES BUREAU OF MINES,
ADVISORY BOARD OF COAL-MINE OPERATORS
AND ENGINEERS.

SOME FACTORS IN THE SPONTANEOUS COMBUSTION OF BITUMINOUS COAL.

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CARNEGIE INSTITUTE OF TECHNOLOGY,
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PREFACE.

Pittsburgh is the greatest industrial center in America, and the heart of the greatest bituminous coal-mining district in the world. It is eminently desirable, therefore, that this city should have an institution which devotes a part of its great facilities to the scientific study of that branch of the industry which is largely responsible for Pittsburgh's development and that of Western Pennsylvania.

On May 27, 1919, a number of leading representatives of the coal-mining industry of Western Pennsylvania met in conference with the then President of the Carnegie Institute of Technology with a view of bringing about closer relations between the Institute and the mining interests. It was felt that the advice and co-operation of men in the field were necessary for the training of young men for mining work, and at the conclusion of the meeting the following resolution was adopted:

> That this gathering give its approval and moral and material support to the form of education proposed for the Carnegie Institute of Technology by which students may receive a combined technical, practical, and business training, necessary to fit them for service in the coal mining and allied industries. Further, that the President of the Carnegie Institute of Technology appoint a board of no less than ten men representing the coal mining and allied industries, the United States Bureau of Mines, the State Department of Mines, and the Carnegie Institute of Technology, who will advise and assist in carrying out this program of education and training, particularly in its practical phases to the mining industry and in its cooperation with the United States Bureau of Mines.

Following further the intention of this resolution, the President of the Institute entered into a co-operative agreement on June 1, 1919, with the Director of the United States Bureau of Mines whereby full advantage could be taken of the Bureau's laboratories, equipment, and library, as well as of the advice and instruction of its technical staff.

To carry out this new program there was organized during the summer months the Cooperative Mining Courses in the Department of Mining and Metallurgical Engineering, College of Engineering, of the Institute. The course in mining engineering covers four years, and leads to the degree of Bachelor of Science. The two-year course in coal mining is planned to prepare men with a certain amount of practical experience for executive positions. The four-weeks intensive summer course in coal mining is designed for miners who aspire to be firebosses and mine foremen. In a large measure, the new mining, ore-dressing, and coal-washing laboratories at the Institute have been equipped gratuitously by various manufacturers of mining machinery and appliances. Co-operative research through teaching and research fellowships is devoted to various problems in coal mining and the utilization of fuels. The Institute selects the fellows, the Bureau of Mines provides the laboratory facilities and the Advisory Board determines what problems be undertaken, and publishes the reports.

The primary object of this co-operation of the Carnegie Institute of Technology, the United States Bureau of Mines, and the Advisory Board of Coal Mine Operators and Engineers is the proper education and training of young men for the mining industry. The ultimate objective is to bring about better conditions and greater efficiency in mining operations. The decrease in reserves of coal and increasing cost of production make it urgently necessary for mine operators and engineers to take advantage of everything which modern science, machinery, and methods can contribute.

EDWARD STEIDLE,
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FOREWORD.

The investigation described in this paper was conducted by the Cooperative Mining Courses, Department of Mining, Carnegie Institute of Technology, and the Pittsburgh Experiment Station of the U. S. Bureau of Mines, in co-operation with the coal mining industry of Western Pennsylvania. Under co-operative agreement, four research fellowships paying $750 per annum per year of ten months, are supported by the Carnegie Institute of Technology. These fellowships are open to properly qualified graduates of universities and technical schools. The research work is carried on in the laboratories of the Bureau of Mines, under the direction of a member of the Bureau research staff and is published under the joint authorship of the two investigators.

Fellowship holders are required to register at the Institute as graduate students, and become candidates for the degree of Master of Science, unless an equivalent degree has been previously earned. The purpose of these fellowships is the solution of problems in mining and the utilization of coal.

The study of factors in the spontaneous combustion of bituminous coal was undertaken at the suggestion of the Advisory Board of coal operators with a view to obtaining more experimental information on the reasons why certain coals have a greater tendency than others to fire spontaneously in storage. A laboratory test for determining the relative tendency for spontaneous firing was devised, and this "critical temperature" test was applied in studying the factors in spontaneous combustion. The authors have shown that fine coal dust and moist air quickly increase the hazards of spontaneous combustion. Mixing fresh coal and old coal does not develop any more heat than that due to the coals themselves when piled separately.

The "anthraxylon" or "woody" constituents of the coal show a definitely lower critical temperature, and therefore are probably more responsible for spontaneous combustion than the "attritus" constituents of coal. However, more investigation is required to isolate and evaluate the easily oxidizable constituents of coal.

The "critical temperature" method of testing coal may be applied to the various coals of the country for grading their relative tendencies to fire spontaneously, and the Bureau of Mines expects to develop this method further and apply it in a survey of the coals of the United States.

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The writers wish to express their appreciation for the helpful suggestions of A. C. Fieldner, superintendent and supervising chemist, Pittsburgh Experiment Station, and O. P. Hood, chief mechanical engineer, U. S. Bureau of Mines; also for the co-operation and assistance rendered by Edward Steidle, supervisor, Cooperative Mining Courses, and by officials of the mines from which samples were procured.

SOME FACTORS IN THE SPONTANEOUS COMBUSTION OF BITUMINOUS COAL.

By JOSEPH D. DAVIS *and* JOHN F. BYRNE.

INTRODUCTION.

Safe storage of bituminous coal is probably the only solution of the problem of stabilizing the coal industry. As long as the peaks of demand react back to the miners, the industry will be a seasonal one, with a resultant unsatisfactory labor situation. If some system could be devised whereby coal could be stored economically, with little deterioration and danger of spontaneous combustion, the mines would be operated practically the whole year—say, 300 working days, instead of 180 to 270 days as in 1920—at a uniform rate of production. Unfortunately, no such general storage system has yet been devised.

The loss by deterioration of coal at ordinary temperatures is small when compared with that caused by rapid oxidation at elevated temperatures and the loss by spontaneous ignition. To overcome the hazards of self-heating and spontaneous combustion, various means of storage have been suggested, such as storing under water or in an atmosphere of carbon dioxide; screening the coal and storing only large sizes; cooling the coal pile by means of ventilating pipes; covering the coal pile with sand or with a layer of fine coal to prevent breathing of the heap, and so forth. Many of these methods do more harm than good, and others are prohibitive on account of their cost.

Much has been written on the causes of spontaneous combustion, but the literature is so contradictory that one does not know which theory to accept. This divergence of opinion is accounted for by the complexity of the actions taking place in the coal pile, each one of which must be considered in the final estimation of the danger of ignition.

SCOPE OF INVESTIGATION.

In this paper are considered a few factors which bear on the problem, also a resume of the work of previous investigators on these particular factors. Briefly, the following shows what has been done in this investigation:

1. Coals, under various physical and chemical conditions, have been tested to determine the temperature at which they generate heat so rapidly that, provided no deterrent is applied, the

coal will eventually ignite. This temperature has been arbitrarily called the "critical temperature." Under similar conditions of heating and aerating, this critical temperature is an index of the liability of a coal to fire spontaneously.

2. The critical temperatures of various sizes of fine coal have been determined and the ratio between size of coal particles and surface area has been measured.

3. The influences of moist and of dry air have been compared.

4. The critical temperature of pyrite, pyritic coal, and mixtures of coal and pyrite have been measured.

5. Mixtures of fresh and oxidized coal have been tested to determine whether or not the storage of coal at different times on the same coal pile lowers the critical temperature of the mixture below that of the poorest coal present, and increases the hazard of spontaneous combustion.

6. The heat conductivity of different sizes of coal has been measured as an index of the rate of dissipation of the heat generated in a coal pile.

7. The amount of heat lost by coal through oxidation for a fixed time at a fixed temperature has been accurately determined.

8. From the heat generated and the rate of heat dissipation it is possible to determine if a coal will fire spontaneously under fixed conditions.

While these factors are not the only ones affecting the heating of coal, they have been generally considered as having an important bearing thereon.

DEVELOPMENT OF APPARATUS.

Various devices have been recommended for testing coals for spontaneous combustion, the majority being based on the principle of determining the amount of oxygen absorbed by a coal sample under fixed conditions of temperature and pressure. While accurate results on the oxygen absorption capacity of different coals have been obtained, it is difficult to correlate this with the actual tendency of a coal to fire spontaneously. It seems as though a more logical test is one that measures the temperature at which the coal begins to generate heat at such a rate that it will eventually ignite, provided that no preventives are used.

Since heat is generated in coal at ordinary temperatures, the coal would eventually ignite provided it was perfectly insulated and there was a sufficiency of air present. The time required in each case would be an indication of the relative tendencies of coals to fire spontaneously. However, in many cases, the time would be long, sometimes almost indefinite, so such a test would be impractical for laboratory procedure. With a rise in temperature, the rate of heat generation is rapidly increased. If the temperature of the coal is raised at a uniform rate from an external source, and the air is preheated to the temperature of the coal, eventually a point will be reached at which the internal heat of the coal will cause it to rise rapidly above the temperature applied. From that point it is only a matter of time until the coal will ignite. This critical temperature at which rapid self-heating of the coal begins, varies for different coals and for different conditions with the same coal, and is, no doubt, an indication of the probability of the coal firing spontaneously. Of course, it is not true that coal is free from all danger of ignition below its critical temperature, but, under similar conditions, the coal having the lower critical temperature is more inclined to spontaneous combustion.

In order to determine this critical temperature, a heating apparatus was constructed (See fig. 1 and 2.) The heating oven—the external source of heat—consisted of a tube wound with nichrome resistance wire, and insulated by a coating of asbestos paper. The heating current was applied by a 110-volt direct current line. Inside the furnace was a pyrex tube—14 inches long and 2 inches in diameter—the lower part serving as a reservoir in which the air was raised to the temperature of the furnace before striking the coal. Into the upper part of this tube was fitted a smaller pyrex tube—6 by 1¼ inches—in which the coal was placed. The junction between the two pyrex tubes was closed by a rubber seal, so that all the air entering the outer tube passed through the coal in the inner tube. A copper-constantin thermocouple was placed in the air stream just below the coal, and another similar couple was put in the center of the coal mass. These led to a Leeds-Northrup potentiometer indicator, on which the temperatures of the air and coal were read. Fastened to the lower end of the small tube was a five-element couple—five junctions in the coal, and five in the air immediately below. The leads from this couple were connected to a Thwing automatic temperature controller, which made contact every half minute. When the temperature of the coal rose above that of the intake air, the controller was thrown over, thereby closing a switch which short-circuited a resistance in the heating line. The point at which this switch was thrown was taken as the "critical temperature" in these experiments. This increased the heating rate of the oven, causing it to follow more closely the rapid self-

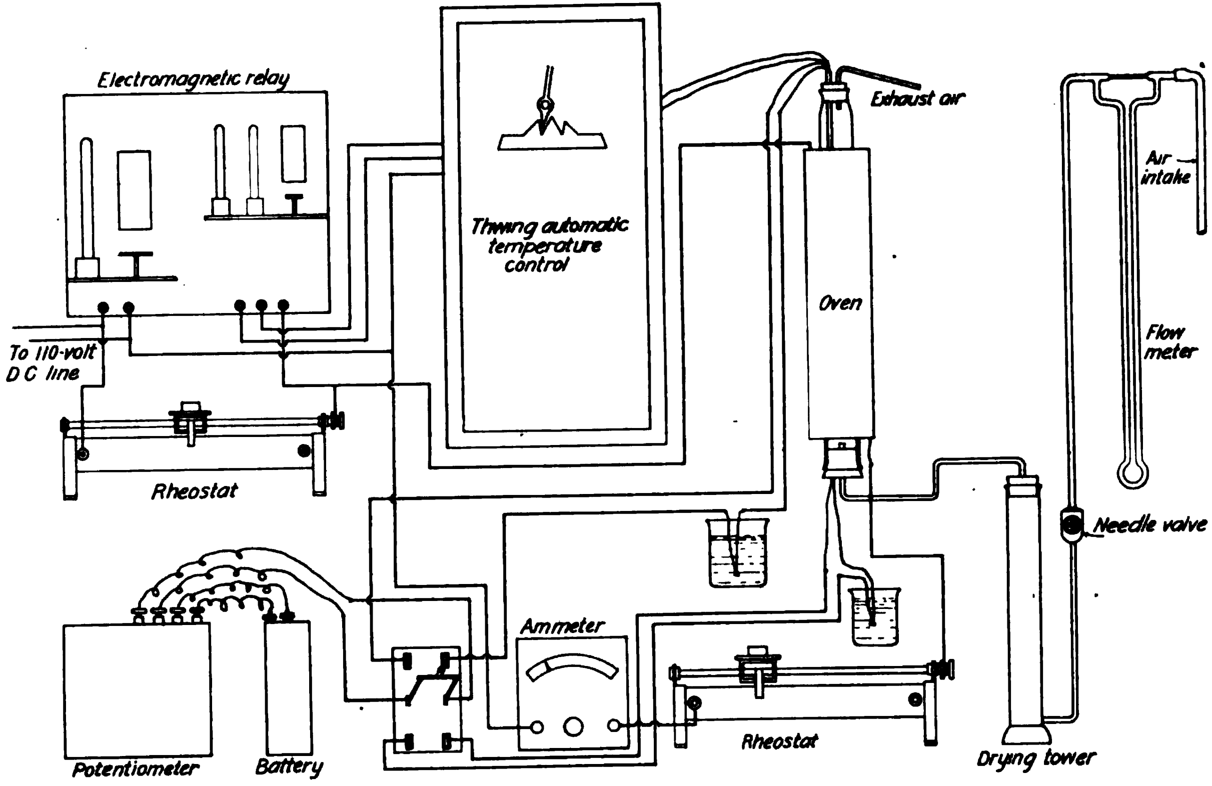

FIGURE 1.—*Apparatus for obtaining critical temperature of coal.*

heating of the coal. However, the coal heated at such a rate that it was impossible to keep the oven and the coal at equal temperatures indefinitely.

The air flow was controlled by a needle-valve and measured by a flowmeter. A water-bottle could be inserted in the line when it was desired to have the air saturated with moisture, or a series of calcium chloride towers when it was desired to have the air absolutely dry.

The coal to be tested was placed in the inner tube, 6-gram samples making a bed 1½ inches deep. This was held in place by mats of glass wool. The oven was heated at a uniform rate, and the temperatures of the air and coal were read at regular intervals, so two time-temperature curves were obtained (fig. 3). At low temperatures these curves were parallel, but at higher temperatures the coal heated more rapidly than the oven, until additional current was thrown on, as explained above. Then the coal and air temperatures rose at the same rate for a short interval, after which the coal heated so rapidly that the oven could no longer follow.

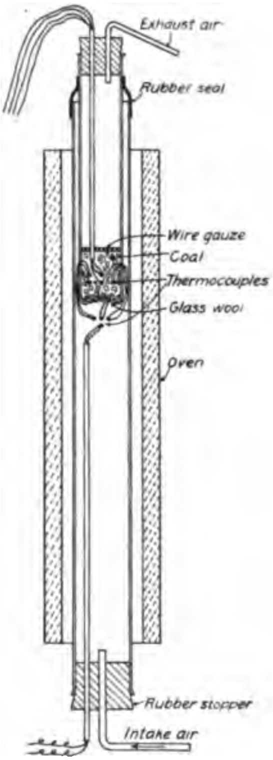

FIGURE 2.—*Section of heating furnace and tubes.*

Although no doubt heat is generated in the coal at temperatures lower than that given by the intersection of the time-temperature curve of the coal, and that of the air stream, yet it is not until this point is reached that the generated heat is rapid enough to lead to subsequent ignition. If the external source of heat is removed before the critical temperature is reached, the coal curve would approach the air curve much more slowly, and the critical temperature, approximately the same as previously obtained, would not be reached until some later time. The critical temperature is not an absolute figure by any means, but only an empirical temperature which serves as a basis of comparison for the spontaneous combustion proclivities of various coals.

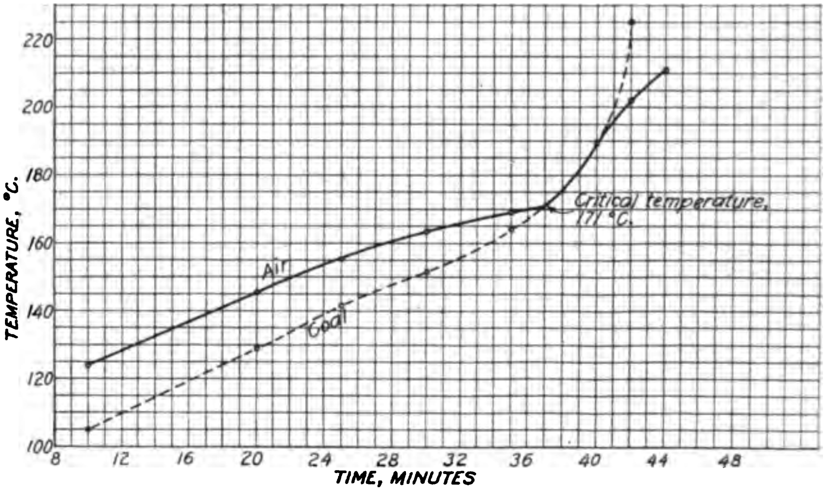

FIGURE 3.—*Critical temperature of 200-mesh Freeport coal.*

EFFECT OF SIZE OF COAL.

The presence of slack and fines has been almost universally recognized as a source of danger in coal piles. That fines weather more than lump coal was recognized by Grundmann[1] as early as 1862. Richters[2], in his experiments during 1868, proved this conclusively, and since that time experimenters have continually cautioned against the storage of small coal, either separately or mixed with lump.

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[1] Carnall Zeitschrift, vol. x, 1862, p. 236.

[2] Dinglers Poly. Journal, vol. 190, 1868, p. 398; vol. 193, 1869, p. 54, p. 264; vol. 195, 1870, pp. 315-449.

Winmill[3] found that in a long period, the total amount of oxygen absorbed is practically independent of the state of division of the coal. Oxidation is not simply a surface action. Although coal is highly impervious to gases[4] even under a pressure of one atmosphere, yet the oxygen in some manner penetrates the coal particles. The following table shows the results obtained by Winmill[5] on the comparison of rate of oxidation of coal and size of coal particles:

Size of coal and rate of oxidation thereof.

	—200 mesh.	—30 + 60 mesh.	—10 + 30 mesh.	—2 + 10 mesh.
Approximate ratio of surfaces.............	100	20	7.5	1.7
Rate of oxygen absorption on fresh samples.............	100	60	40.0	6.0
Average ratio of absorption during the first 96 hours........	100	80	72.0	27.0

The rate of heat production for lump coal is much slower than for fines, and the heat has more chance to be dissipated. The rate of absorption of oxygen decreases as the fineness of the particles decreases.

Coal should be handled as little as possible to prevent disintegration. Fires on coal vessels have occurred most commonly under the hatchways, where the fines accumulate. Vaughan[6] says that the dust constituents are mainly pyrite and fusain (mineral charcoal), "the latter serving as touchwood or tinder. Coal splits along layers of fusain and pyrite, so large amounts of these will be in the dust. Undried pyrite and fusain are heavier than coal, and hence are collected by gravity." The fines will settle toward the bottom and center of the pile, where conditions for spontaneous heating are most favorable. The surrounding coal makes an excellent insulation, and the air, while present in sufficient quantity for the oxidation of the coal, is adequate to carry away but a small amount of the heat generated.

Covering the pile with a layer of fine coal, and filling the interstitial spaces of the pile with slack have been suggested as safe methods for storing coal, but neither of these has proved successful.

Wheeler[7] made a series of tests on the friability of various coals by grinding samples in a ball-mill for a fixed time and at a fixed speed. The relative amounts of fines formed under identical conditions determined the friability of the coal. The coals with high friability generally had low oxygen content, and vice versa, showing that a tendency to self-heating due to high oxygen content is generally counterbalanced by low friability and resistance to grinding.

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[3] Winmill, T. F., Trans. Inst. Min. Eng., vol. 51, 1916, p. 493.

[4] Graham, J. K., Trans. Inst. Min. Eng., vol. 52, 1917, p. 338.

[5] Loc. cit.

[6] Vaughan, J. A., Spontaneous combustion: South African Min. & Eng. Jour. Coal Number, July, 1921, p. 190.

In order to determine the influence of fines in a coal pile, and the relative sensitivities of different sizes, various samples were tested in the apparatus previously described. Air saturated with moisture was used. The coal tested was of the lower bench of the Freeport seam. The following critical temperatures were obtained:

Influence of size of coal on critical temperature.

Size, mesh.	Critical temperature, °C.
— 10 + 20	231
— 20 + 35	228
— 35 + 60	198
— 60 + 100	184
—100 + 200	181
—200	171

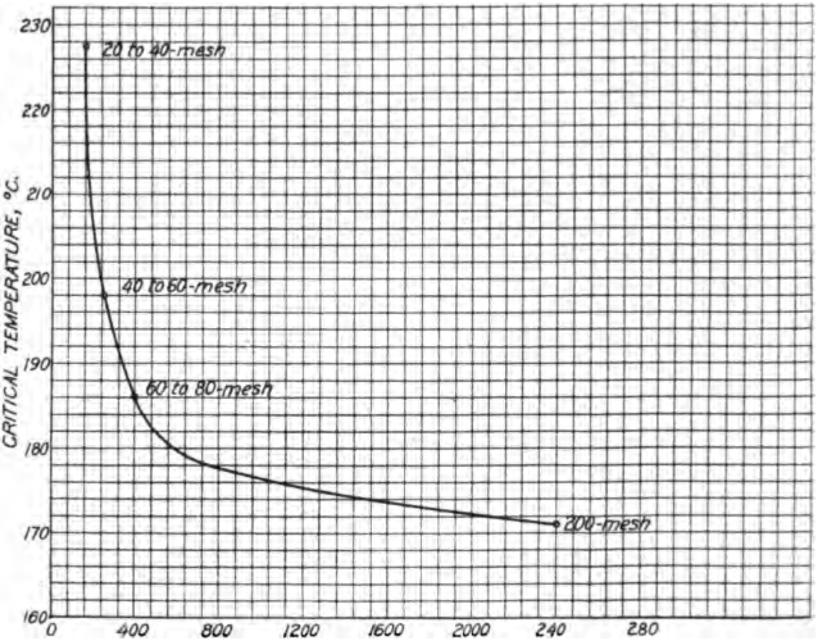

FIGURE 4.—*Relation between surface area and critical temperature of upper bench Freeport coal.*

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[7] Wheeler, R. V., Colliery Guardian, vol. 122, 1921, p. 516.

Figure 4 shows the relation between the critical temperature and the exposed surface of the coal, and figure 5 shows the relative rates of heating in —10 + 20 mesh and —200 mesh coal.

The samples used were from the Creighton mine, Creighton, Pa. They were sealed in air-tight jars at the mine. In the laboratory they were crushed and sized as quickly as possible, and kept in closed bottles until the tests were made. The analysis of the coal in these tests was as follows:

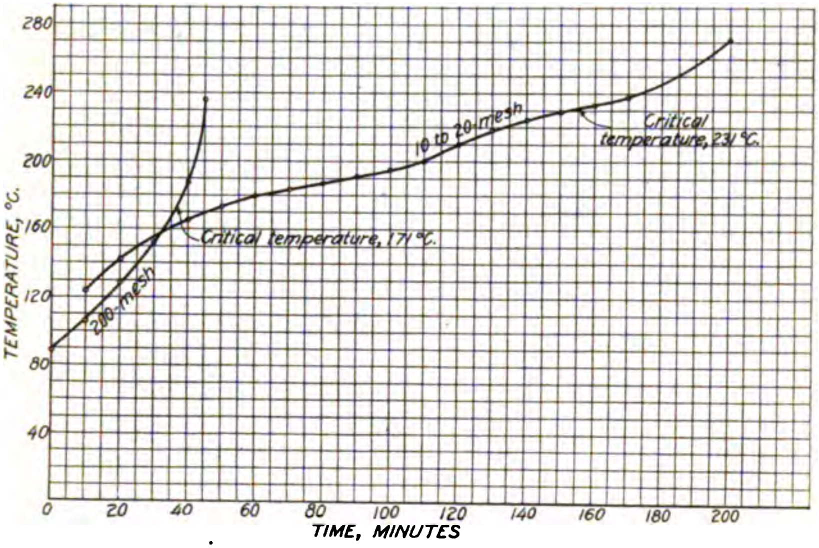

FIGURE 5.—*Relative heating rates of 200-mesh coal and 10 to 20-mesh coal.*

Analysis of coal from Creighton, Pa. (as received.)

Proximate analysis.	
Moisture	1.3
Volatile matter	35.4
Fixed carbon	55.0
Ash	8.3
Calories	7567
B. t. u.	13620

Ultimate analysis.	
Hydrogen	5.2
Carbon	75.9
Nitrogen	1.6
Oxygen	6.9
Sulphur	2.1

The more rapid oxidation and self-heating of fine sizes of coal is due, not to the smaller volume of the particles, but to the fact that more surface is exposed to the action of the air. If a ton of coal could be delivered in a single cube, each dimension would be 2.8 feet[8]. If this cube, having an original area of 47 square feet, be continuously subdivided, the surface rapidly increases until at about 16 mesh there is an acre of exposed coal surface. The great increase in extent of surface does not begin until below 1¼-inch nut. However, coal does not break in the form of perfect cubes. To determine more accurately the exact surface exposed the procedure was as follows:

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[8] Hood, O. P., Factors in the spontaneous combustion of coal: Bureau of Mines Technical Paper 311, 1922, 9 pp.

The specific gravity of a fine coal sample was accurately determined. An actual count of the particles in a closely sized sample was made. Then a large number of particles were measured by means of a micrometer microscope, and their average shape determined. These range from irregular prisms to thin plates of various dimensions. The predominating figure for this particular coal was one bounded on the two major sides by isosceles triangles, and on the three minor sides by rectangles. The ratio of base of the triangles to the side is about 3:5, and the altitude of the rectangle is about one-fifth of the base of the triangle. Thus, the area of each particle is the summation of the areas of two equal isosceles triangles; two rectangles, of which the length of each is equal to a side of the triangle and whose altitudes is one-fifth of the base of the triangle; and one rectangle with the same altitude as the other two rectangles, and with a length equal to the base of the triangle. The area of an average particle was calculated and also the total area per gram.

A second method was used to check this calculation. The volume of a particle was first calculated, and from this the volume of a gram was determined. This, multiplied by the specific gravity of the coal should, of course, give unity.

A third check was made on the ratios between areas of the different sizes by means of a turbidimeter. It is obvious that with regular figures, the opacity of a suspension of fine particles in a liquid is proportional to the average area of the major planes of the particles interposed, and that this area is also proportional to the total surface area of the particles. This will be made clear on the examination of several well-defined geometric figures as spheres, prisms, tetrahedrons, etc. In a sample of particles containing a variety of shapes, the same reasoning will apply, but it is impossible to determine the constant of proportionality. In two different samples of different sizes, but of the same substance, as in the case of several samples of the same coal, it is reasonable to assume that the proportionality constant for one size will agree very closely with that constant for another. Therefore, the opacity of a solution in which particles of coal are suspended should vary inversely with the area of the particles, and it is only necessary to determine the relative weights of different sizes of coal having the same opacity to determine the ratio of their exposed areas.

The turbidimeter used to compare the areas of different sizes of coal consisted of two vertical tubes, both having small tubes sealed in the bottom and the top of the first being connected to the bottom of the second by means of a glass tube. Both tubes were filled to the same level with xylol. Into the first tube a gram of coal, accurately weighed and carefully sized, was placed. Then a current of air was bubbled through the solution containing the coal in the first tube. Since the tubes were in series, the air-flow through each was the same. The coal whose surface area was desired was added to the second tube, until the light traveling through the two tubes was the same. Then the amount of coal added to the second tube was determined. As previously stated, the areas of the two sizes of coal are inversely proportional to weights required to obtain the same opacity. The ratios of sizes whose areas had been measured checked fairly well with the ratios obtained by the turbidity method. This also is a means of obtaining areas of sizes too fine for actual measurement. Following are the data secured on the surface area measurements:

Surface area measurements of coals.

Size, mesh.	Long dimension, mm. (a)	Short dimension, mm. (b)	Number, per gram.	Surface, per particle, sq. mm.	Surface, per gram, sq. cm.
20 to 40	1.199	0.814	8,740	1.584	138.4
40 to 60	0.692	0.448	50,192	0.500	251.4
60 to 80	0.498	0.319	157,013	0.253	396.4
—200	(determined by turbidimeter)				2499.1

Volume of one particle = (½ a b) (0.224 b)
Specific gravity of coal used = 1.27.

Size, mesh.	Volume, per particle, mm.^{3}	Volume, per gram, c.c.	Volume, per gram, x 1.27. (should be 1.00)
20 to 40	0.69	0.78	1.00
40 to 60	0.15	0.78	1.00
60 to 80	0.057	0.89	1.13

The volume of 60 to 80 mesh as calculated is 13.0 per cent too high.

The ratios of areas as determined by the turbidimeter were as under:

Sizes.	Calculated.	Determined.
$\frac{20-40}{40-60}$	$\frac{0.55}{1}$	$\frac{0.65}{1}$
$\frac{40-60}{60-80}$	$\frac{0.63}{1}$	$\frac{0.61}{1}$
$\frac{40-60}{-200}$	$\frac{....}{....}$	$\frac{0.1006}{1}$

The surface area per gram of —200 mesh coal is 2499.1 square centimeters.

From this it is evident that the surface exposed increases rapidly with the finer sizes (figure 6), and a small amount of fines in a coal pile may bring the surface exposed up to dangerous areas. For example, 3.7 pounds of —200 mesh coal have as much surface as a ton of coal in 3-inch lumps: and 23 pounds of 60 to 80-mesh coal or 67 pounds of 20 to 40-mesh are also equivalent in surface to a ton of 3-inch lumps. Not only is the heat generated more rapidly in these fine sizes, but also it is dissipated much more slowly. There is no doubt that one means of reducing the danger of spontaneous combustion is to prevent the segregation of fines in the coal pile: or, better, to store only coarse sizes of coal.

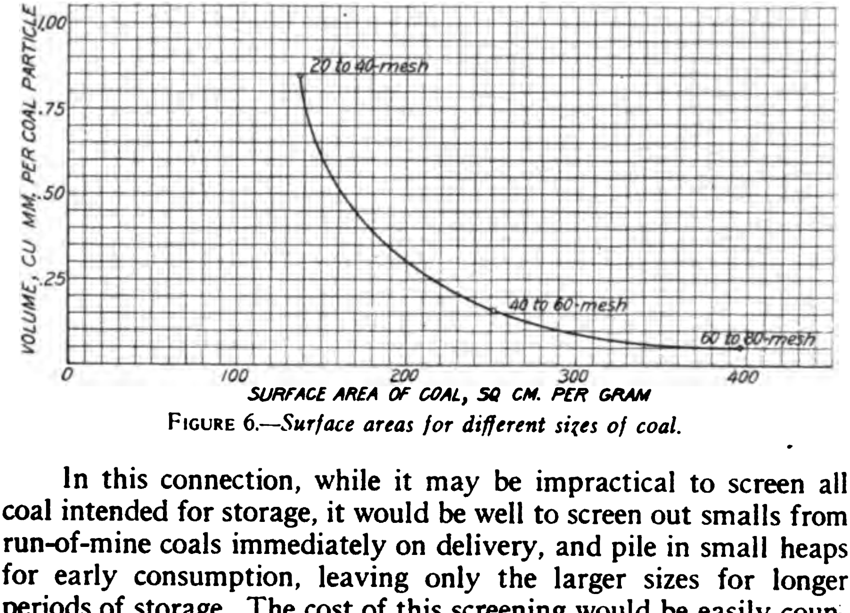

FIGURE 6.—*Surface areas for different sizes of coal.*

In this connection, while it may be impractical to screen all coal intended for storage, it would be well to screen out smalls from run-of-mine coals immediately on delivery, and pile in small heaps for early consumption, leaving only the larger sizes for longer periods of storage. The cost of this screening would be easily counterbalanced by the additional safety of the entire stock.

EFFECT OF MOISTURE.

The role of moisture in the spontaneous heating of coal has been discussed by many investigators, who differ widely in their conclusions. Richters[9] found that air-dried coal absorbed oxygen more quickly than moist coal. He also found that by placing small bulbs containing fused calcium chloride beside the dry sample of coal, so that it gradually became dryer, the rate of absorption was increased.

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[9] Dinglers Poly. Jour., vol. 190, 1868, p. 398; vol. 193, 1869, pp. 54 and 264; vol. 195, 1870, pp. 315 and 449.

Fayol[10] tested coals under three separate conditions of moisture, namely:

(1) Freshly won fines; (2) the same coal dried in ovens at a temperature not exceeding 40° C., and (3) the same coal not dried, but sprinkled to make it damp, but not wet. The behavior of the different piles, both wet and dry, was almost identical.

Doane[11] stated that the amount of moisture present in a bituminous fuel after drying in the air is a measure of the risk of spontaneous ignition when the fuel is stored; coals containing more than 4.75 per cent of moisture are dangerous.

Parr and Kressman[12] experimented on the rate of heating of both dry and thoroughly wet coal and concluded that "any coal with conditions favorable to oxidation will be facilitated in that action by the presence of moisture. Without exception, in all series of tests, the wetting of the coal increased the activity as shown by the ultimate temperature."

Porter and Ovitz[13] reported that they had found no case of spontaneous combustion in which it could be proved that moisture had been a factor; however, moisture might cause the closer packing of fine coal and thus facilitate spontaneous combustion.

Mahler[14] found that coal in the presence of oxygen under pressure absorbed a considerably larger quantity when wet than when dry.

Winmill[15] found that coal, when moist, absorbed oxygen more rapidly than when dry. Graham[16], after his experiments on the influence of moisture on the rate of oxygen absorption, arrived at some rather startling conclusions, as follows:

> These results show conclusively that the rate of oxidation of moist coal dust at 30 and 50° C. in a current of air saturated with moisture, is much greater than that for a portion of the same sample oxidized when dry, the rates of oxidation in the two cases being on the average approximately as 1.5 to 1.

Drakeley[17], in writing on the effect of pyrite, said:

> A moist atmosphere is practically essential for the oxidation of iron pyrites. Moisture accelerates the oxidation of coal, but an excessive amount of water retards spontaneous combustion in two ways: first, the water enters the pores of the coal, and so renders it less pervious to air; and secondly, the temperature is kept low by evaporation.

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[10] Etudes sur l'alteration et la combustion spontanee de la houille exposee a l'air, 1879, p. 155.

[11] Doane, A. O., Eng. News, vol. 52, 1904, p. 141.

[12] Univ. of Illinois, Eng. Exp. Sta. Bull. 46, 1909.

[13] Porter, H. C. and Ovitz, F. K., Bureau of Mines Tech. Paper 16, 1912, 14 pp.

[14] Mahler, M., Colliery Guardian, vol. 106, 1913, p. 891.

[15] Winmill, T. F., Trans. Inst. Min. Eng., vol. 48, 1914, p. 503.

[16] Graham, J. I., Trans. Inst. Min. Eng., vol. 49, 1914, p. 35.

[17] Drakeley, T. J., Colliery Guardian, vol. 112, 1916, p. 762.

There is no doubt that moisture facilitates the oxidation of iron sulphide (pyrite)—in fact, in dry air, pyrite is scarcely affected. It is undecided, however, whether heat generated by the oxidation of the pyrite is sufficient to counteract the heat lost by the vaporization of the moisture.

Porter and Cameron[18], in their experiments on Canadian coals, arrived at the following conclusions:

> Oxidation depends largely upon the presence of moisture. With absolutely dry gas and almost dry coal, some oxidation does take place, but it is clear that moisture greatly facilitates the reaction. Too much moisture will undoubtedly hinder the oxidation and consequent production of heat, and it must be quite clear that nothing in the experiments goes to indicate that 'wet' coal oxidizes more rapidly than 'dry,' using these terms in the ordinary commercial sense. The 'wet' tests were really 'dry,' in the sense that the coal had been dried to above the boiling point of water, and the only moisture admitted was that of the air saturated by passing through water. The total amount of moisture was therefore much lower than in any industrial dry cold storage. On the other hand, the dry tests as conducted involve an almost absolute exclusion of moisture, a condition quite impossible except in an elaborate laboratory experiment.

R. V. Wheeler, before the British Committee on Spontaneous Combustion of Coal in Mines, testified that the percentages of moisture contained in a coal has but little effect in respect of self-heating, but he would not say that it had no effect. The conclusion of this Committee in regard to moisture is:

> That the presence of moisture in coal has an accelerating effect on its oxidation, and consequently that coals high in hygroscopic moisture absorb oxygen more readily than those of low moisture content.

In actual storage, neither the coal nor the air in contact with it is absolutely dry or completely saturated with moisture. To approximate storage conditions, a sample of coal, freshly mined, was treated with dry air, and another sample treated with air saturated with moisture, in the apparatus previously described. For the dry test, the air was passed through two drying towers containing calcium chloride, and for the wet test, the air was bubbled through water at atmospheric temperature. Following are the results obtained:

	Dry air, °C.	Saturated air, °C.
Freeport seam, upper bench, —200 mesh	171	166
Freeport seam, lower bench, —200 mesh	174	171

The critical temperature, in dry air, is higher than that in saturated air, and the rate of temperature increase, after the critical point is reached, is slower in an atmosphere of dry air, as illustrated in figure 7. From this it appears that moisture has an accelerating effect on the spontaneous heating of coal. The tests did not show a retardation of the heating rate of the coal at 100° C., owing to the evaporation of the water, contrary to what would be expected.

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[18] Porter, J. B., and Cameron, A. E., Weathering of coal: Canadian Dept. of Mines, Bull. 338, 1915.

From the opinions of the majority of experimenters, and from the results of these experiments, moisture, both in the coal itself and in the air surrounding the coal seems to be an important factor.

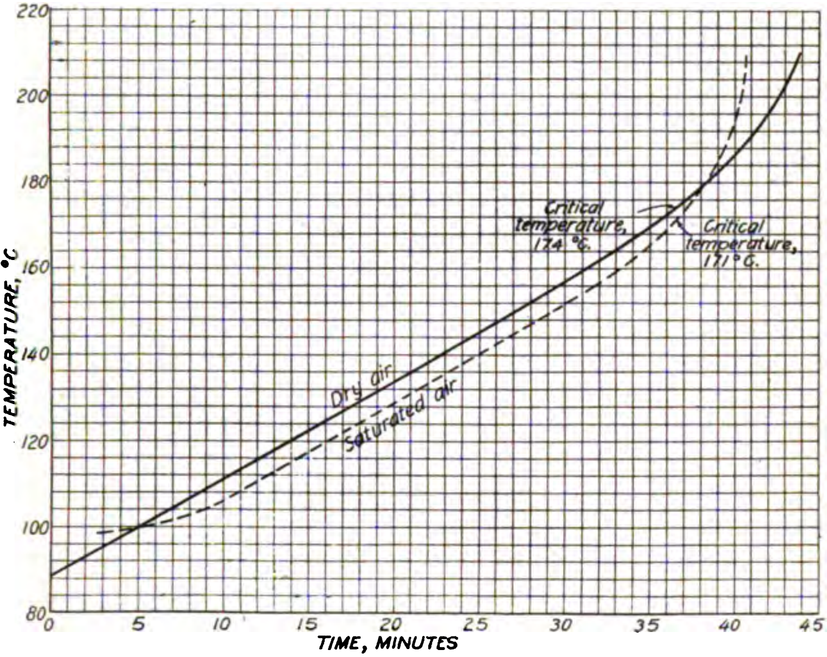

FIGURE 7.—*Lower bench, Freeport seam, 200-mesh, freshly mined, sample* 185 *c.c. of air per minute.*

EFFECT OF PYRITE.

Opinions differ considerably concerning the part played by pyrite in the spontaneous combustion of coal. The earliest writers considered pyrite (or "brass lumps" or "coal brasses") the sole cause of spontaneous fines in coal. As far back as 1686, Dr. Plott, keeper of the Ashmolean Museum and Professor of Chemistry in the University of Oxford, England, in his "Natural History of Staffordshire," wrote of a fire that he attributed to the heating of pyrite, which, in turn, ignited the coal.

About 1800, Berzelius[19], the Swedish chemist, again suggested that the heat evolved by the oxidation of pyrite might have an important bearing on spontaneous combustion. Finch[20] in 1818 wrote an account of a "pseudo-volcano" which he attributed to pyrite and to the sulphur contained in the coal. Bald[21] also blamed pyrite as the cause of trouble, but also observed that air and moisture were necessary to generate heat.

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[19] Lewes, V. B., The spontaneous ignition of coal; British Assoc. for Adv. of Sci., Aug. 1891, p. 602.

[20] Finch, John, Magazine of Chemistry, Mineralology, Mechanics, Natural History, Agriculture, and the Arts, vol. xi, 1818. Article iv., p. 342.

Richters[22], as a result of his extensive experiments in 1868 and 1870, believed that the heat generated by oxidation of pyrite has a subsidiary part in the spontaneous ignition of coal. He was the first to recognize the mechanical results of oxidation of pyrite in effecting disintegration of the coal, thereby increasing its perviousness and hastening oxidation. Moisture facilitates oxidation of pyrite.

The Royal Commission, in its report of 1876, on "Spontaneous Combustion of Coal in Ships," ascribed spontaneous combustion partly to pyrite. In 1879, Kimball[23], of Lehigh University, said that the weathering of pyrite and marcasite (white iron pyrite) is of as much importance as the weathering of the coal itself. This is the first time that any distinction was made between pyrite and marcasite in coal. In the same year, Fayol[24] concluded that admixture with pyrite did not hasten spontaneous heating, but that pyrite had an indirect influence in breaking down the coal.

Haedicke[25] in 1880 assigned to pyrite the leading part in spontaneous ignition.

In 1890, Lewes[26], in the result of investigation into fires on coal ships, stated that the oxidation of pyrite plays only a subsidiary role in regard to heating, but as it becomes oxidized, it swells and causes the coal to disintegrate, thus exposing new surfaces to the action of oxygen. Some of the coals most prone to spontaneous combustion contain only 0.8 per cent pyrite. If 100 pounds of the coal were taken, and the whole of the pyrite in it concentrated in one spot and rapidly oxidized to the sulphate condition, the temperature would barely be raised to 100° C., if all loss of heat could be avoided.

Fischer[27], in 1901, again discusses the distinction between marcasite and pyrite, believing the former easier to weather than the latter.

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[21] Bald, Robert, The Edinburgh New Philosophical Journal, April-September, 1828.

[22] Dingler's Poly. Jour., vol. 190, 1868, p. 398; vol. 193, 1869, pp. 54 and 264; vol. 195, 1870, pp. 315 and 449.

[23] Kimball, James P., Trans. Amer. Inst. Min. Eng., vol. 8, 1879, pp. 204-225.

[24] Etudes sur l'alteration et la combustion spontanee de la houille exposee a l'air. 1879.

[25] Dingler's Poly. Jour., vol. 239, 1881, pp. 148-149.

[26] Jour. Soc. Arts, vol. 40, 1892, pp. 352-365; Jour. Gas Lighting, vol. 55, 1890, p. 145.

[27] Die Brenstoffe Deutschlands, 1901, pp. 1-107.

Dennstedt and Bunz[28], in 1908, deny that either the amount or kind of mineral substance or pyrite found in coal has any effect on the self-heating. Threlfall[29], in 1909, pointed out the fact that no connection has ever been traced between the pyritic content of coal and the frequency of fires. He did not believe that pyrite has any great influence on spontaneous ignition.

Parr and Kressman[30], as a result of their experiments on Illinois coal, arrived at the following conclusions regarding pyrite:

> The presence of sulphur in the form of iron pyrites is a positive source of heat due to the reaction between sulphur and oxygen. This may be conveniently referred to as the second stage in the process of oxidation. Here again, rapidity of oxidation is directly dependent upon fineness of division. Since coals, as a rule, have a much higher earthy or ash content in the fine duff (dust or fine screenings), and since iron pyrites is a large component of this material, it follows that the presence of dust or duff in all coals of the Illinois type is a positive source of danger. Since coals of the Illinois or Mid-Continental field have in a large number of cases, iron pyrites averaging over 6 per cent, or, as sulphur, above 3 per cent, the heat increment from the oxidation of only one-fifth of this material is sufficient to raise the temperature of the mass approximately 70 degrees, assuming there is no loss by radiation. Under usual conditions, and especially considering the greatly accelerated rate of chemical activity accompanying a rise of temperature, this oxidation may proceed with such rapidity that the heating up of the mass will be but little affected by loss of heat due to radiation, except in relatively shallow piles.

Parr and Kressman also added pyrite in varying quantities to coal and subjected the mixture to oxidation. They found that the ratio of oxidized pyrite to total pyrite present remained practically constant, regardless of the total amount of pyrite present. From this it appears that the oxygen penetrates each gram of pyrite to a definite depth.

Lomax[31], in 1914, as a result of his microscopic examinations of coal, concluded that pyrite disseminated through the coal plays a subsidiary part in spontaneous combustion.

Drakeley[32], in 1916, determined the oxidation products of pyrite, coal, artificial mixtures of coal and pyrite, ferrous sulphate, mixtures of ferrous sulphate and coal, and mixtures of sulphuric acid and coal, and found that more pyrite is oxidized when alone than when mixed with coal, due to either the coal acting as a deterrent factor or to poorer ventilation. Saturating coal with ferrous sulphate increased the amount of carbon dioxide evolved. Sulphuric acid reduced the volume of carbon dioxide evolved from coal alone, due, probably, to the acid filling the pores of the coal. Results show that mixing pyrite with coal causes a more rapid absorption at first, but later the rate becomes the same as that of the pure coal. Drakeley suggests that iron pyrite is first oxidized to ferrous sulphate and then to ferric sulphate. This is reduced by contact with the coal. By alternate oxidation and reduction, the iron may act as an oxygen carrier to some particular compound in the coal.

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[28] Zeitschrift fur Ang. Chemie, vol. 35, 1908, pp. 1825-1835.
[29] Threlfall, Richard, Jour. Soc. Chem. Ind., vol. 28, 1909, p. 759.
[30] University of Illinois, Eng. Exp. Station Bull. 46, 1909, p. 52.
[31] Lomax, James, Trans. Inst. Min. Eng., vol. 46, 1913-1914, p. 592.
[32] Colliery Guardian, vol. 112, 1916, p. 762.

When this compound is completely oxidized, the iron ceases to possess catalytic properties, and the oxidation becomes an additive process. Pyrite disseminated through coal in microscopic amounts is more dangerous than the larger nodular pyrite.

The British Committee on Spontaneous Combustion of Coal in Mines, concluded from the evidence presented,

> That some small amount of heat may be developed by the oxidation of pyrites in the coal, when it occurs as an amorphous form of marcasite; but, as pyrites is present in coal in such small proportion as compared to the coal substance proper—which is a bad conductor of heat—the effect of this heat is negligible. The chief part played by pyrites when present in an unstable form is that of a disintegrator of the coal, so rendering the latter more permeable by air, and exposing a greater area of the coal substance to oxidation.

So far as any heating effect of pyrite on coal is concerned, the danger lies, not in the large nodules of pyrite, but in minute particles scattered through the coal mass. Pyrite, finely pulverized and mixed with coal, will not lower the critical temperature of the coal itself, as demonstrated by the following experiment:

A sample of pyrite was taken from the Pittsburgh seam and ground to pass 200-mesh. This was tested for its critical temperature in the apparatus previously described. Then mixtures of Pittsburgh coal and pyrite in various proportions were tested, giving the following results:

	Critical temperature, °C.
Pittsburgh coal, —200 mesh	167
Pyrite, —200 mesh	193
50% coal—50% pyrite	166
33% coal—66% pyrite	167
66% coal—33% pyrite	167

In no case did the presence of pyrite in this form lower the critical temperature of the mixture below that of the coal itself. This, however, can not be taken as conclusive evidence that pyrite is a negligible factor in spontaneous combustion. It is impossible to make up artificial mixtures in which the coal and pyrite are in as intimate contact as they occur in nature. Furthermore, it is impossible to separate the minute particles of pyrite from the coal proper, in order to test identical coals with and without pyrite. A pyritic coal cannot be compared to a non-pyritic coal from another source, as any difference in the rate of spontaneous heating might be due to some constituent other than pyrite, which varies in the two coals. Therefore, the problem of ascertaining the exact function of pyrite in the spontaneous combustion of coal is one of many ramifications.

As already pointed out by several investigators, there is probably a difference in the behavior of pyrite and marcasite in coal. A coal containing bands of marcasite, when exposed to air, will crumble much more rapidly than one containing bands of pyrite. Insofar as affecting disintegration, at least, marcasite is much more active than pyrite. However, it is impossible to distinguish the two in the microscopic nodules which are scattered through the coal, since they have no crystalline form. It may be due to the different heating rates of amorphous pyrite and amorphous marcasite that some coals are more prone to spontaneous combustion than others of the same iron sulphide content.

It is possible that pyrite and marcasite have a catalytic action as suggested by Mahler, acting as an oxygen carrier for some constituent in the coal. Some tests were run using hopcalite* as a catalyzer for the coal, but results were negative, due again, possibly, to failure to get intimate mixtures. The question of pyrite as a catalyzer, and the influence of other catalyzers and methods for obtaining intimate mixtures of the coal and the catalyzers, are problems which merit further investigation. The present consensus of opinion is that pyrite and marcasite play subsidiary parts, but to what extent is not known. When scattered throughout the coal in microscopic particles, they may possibly increase the danger of spontaneous heating, but when present in large lumps, their effect on the heating is negligible.

EFFECT OF MIXING COALS.

It has long been a popular belief among miners and engineers that two grades of coal, or coals from different districts, should not be stored together in the same pile. No definite reason has been advanced why this procedure should increase the risk of spontaneous combustion, and it does not seem logical that two coals mixed together should be more dangerous than the more sensitive one separately. The reason lies probably in the fact that one coal has been partly oxidized, and its temperature raised thereby, at the time the second coal is added to the pile. This makes a heated area near the center of the heap where there is just enough air to continue the oxidation, but where the heat is dissipated very slowly.

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* A mixture of specially prepared manganese dioxide and basic copper carbonate.

Furthermore, the fines from the second coal will filter down to the heated zone, making conditions ideal for spontaneous heating. Hence, the danger of mixing two coals comes not from the nature of the coals themselves, but from the conditions of storage.

According to Porter and Ralston[33], "It is evident that the first step in the oxidation of coal is the formation of an additional compound, or complex, of oxygen with one or more of the substances present in the coal." No carbon dioxide, carbon monoxide, or water is formed. The oxygen apparently attached itself to some unsaturated compound of high carbon content. The resultant compound may not be stable, but may, in turn, surrender its oxygen to the next compound. This interchange of oxygen, accompanied each time by the generation of heat, might be a cause of spontaneous heating of coal.

A fresh coal mixed with a coal partly oxidized might take up oxygen from one of these unstable compounds formed in the first oxidation of the partly weathered coal. The danger in mixing a fresh coal with one which had been stored for a short time might be due to this exchange of oxygen. To determine whether a mixture of fresh and oxidized coal has a lower critical temperature than fresh coal alone, several samples were tested, using the apparatus previously described. The fresh samples were sealed at the mine, and exposed to a minimum amount of air. The oxidized samples were heated in air at 100° C. for periods ranging from 6 to 48 hours, with the results shown in the table following:

Comparative critical temperatures of fresh coal and mixtures of fresh and oxidized coal.

Fresh coal.	50-50 fresh and oxidized coal.	Conditions.
168° C.	174° C.	Oxidized 6 days at room temperature.
168° C.	175° C.	Oxidized 24 hours 100° C.
166° C.	174° C.	Oxidized 6 hours 100° C.
166° C.	174° C.	Oxidized 8 hours 100° C.

The results all show higher critical temperatures for the mixed coal than for the fresh coal alone. Therefore, it would seem that the oxidized coal does not act as an oxygen carrier, but rather as an inert material, whose temperature must be raised by the heat generated in the fresh coal. The danger in storing new coal on an old coal pile seems to be not in the chemical condition of the coal substance itself, but in the elevated temperature of the coal heap at the time and the segregation of fines at the bottom of the second layer or in the middle of the pile as a whole.

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[33] Porter, H. C., and Ralston, O. C., A study of the oxidation of coal; Bureau of Mines Tech. Paper 65, 1914, p. 21.

EFFECT OF DIFFERENT COALS AND COAL CONSTITUENTS.

The tendency of coals to fire spontaneously differs with their age—the younger coals being the most dangerous. No case has been recorded in which anthracite coal fired spontaneously—even fines and slack storing safely. At the other extreme is lignite, which can not be stored, even in lumps, with safety, except under water. Between these two extremes are the various grades of bituminous coals, the class which is most commonly stored. The liability of different bituminous coals to fire varies widely on account of differences in the coal; but, broadly speaking the bituminous coals of the eastern part of the United States store better than the coals of the Middle West. These, in turn, are safer to store than the subbituminous coals of the Intermountain region. While the tendency to fire will vary widely in any one class of coal, generally speaking, the higher the rank the less the danger of fire and the less the deterioration in storage. The classification as to self-heating coincides with the classification of coals, beginning with lignite as the most dangerous, ranging through sub-bituminous, bituminous, semibituminous, and anthracite as the least prone to spontaneous combustion.

The solution of the problem of spontaneous combustion may lie in the microscopic examination of coals and its correlation with the rate of heating. Coal is composed of three parts, namely, anthraxylon, or bright coal, attritus, or dull coal, and mineral charcoal[34], and may be separated into almost pure samples of each. These three constituents differ in their ease of oxidation and rate of heating. When tested in the apparatus previously described, attritus showed a critical temperature of 198° C., while that of anthraxylon was 172° C.—practically equal to the critical temperature of the coal itself. From this it would seem that the anthraxylon is the constituent that heats first in the spontaneous heating of coal.

Mineral charcoal scattered through the coal may be an important factor in this phenomenon. It is more porous than the coal, and therefore presents a greater surface to the action of oxygen. Wheeler and Stopes[35] came to the conclusion "that the critical point in any piece of coal is the juncture between vitrain and fusain, and that fusain is the touch which sets the vitrain on fire." In their opinion, it is particularly dangerous "if the fusain is found embedded in the vitrain. When you find the fusain in juxtaposition, the fusain is most often not in the form of layers in the vitrain, but in pockets." The vitrain is equivalent to the anthraxylon or bright coal, and the fusain is mineral charcoal. Sinnatt[36] found that fusain is the chief constituent of dust in coal mines. It is softer and more friable than the coal proper and therefore would be present in large quantities in the fines in a coal pile. Fusain will ignite and glow at low temperatures, and is readily oxidized at 15° C.

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[34] Thiessen, Reinhardt, Structure in Paleozoic bituminous coals, Bureau of Mines Bull. 117, 1920, 250 pp.

[35] Wheeler, R. V., and Stopes, M., Spontaneous combustion of coal in mines, Final report of Departmental Committee, British Mines Dept., 1921, p. 13.

While anthraxylon has a lower critical temperature than attritus, yet coals in which the former predominates do not have a lower critical temperature. In the case of the Freeport vein, the anthraxylon-attritus ratio decreases from the bottom to the top of the seam. The critical temperatures, however, are practically the same for all parts, as shown in the following table.

	Critical temperature, °C.
No. 1. Cannel roof	177
No. 2. Upper bench	166
No. 3. Lower bench	171
No. 4. Coal below slate bottom	168
No. 5. Coal immediately above fireclay	170

The coal immediately above the fireclay (sample No. 5) is especially rich in anthraxylon, and would be expected to give a much lower critical temperature than the samples comparatively poor therein. The relative amounts of bright and dull bands in a coal cannot be taken as a criterion for its liability to fire spontaneously.

RATE OF HEAT GENERATION AND HEAT DISSIPATION.

Whether or not a coal pile will heat spontaneously depends upon two factors—namely, the rate of heat generation, and the rate of heat dissipation. The time-temperature curve of any heap of coal will depend on the relation between the heat generated and the rate at which it escapes by radiation, convection, and conduction. Unless air can penetrate the pile fast enough to supply fresh oxygen as soon as the existing air is exhausted, the oxidation will cease and the heat which has been generated will diffuse outward. On the other hand, if the air supply is sufficient, oxidation will continue, but the resultant heat will be carried away as soon as it is generated, and no serious rise in temperature will result. The amount of ventilation required to give this cooling effect will, of course, depend upon the rate at which the heat is generated. The heat generated, and consequently the amount of air required for cooling, will increase as the fineness of the coal increases. However, the finer the coal the more difficult it is to supply ventilation, and, therefore, the more difficult it is to carry off the heat formed in fine coal.

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[36] Sinnatt, F. S., loc. cit., p. 14.

O. P. Hood[37] has stated the following in this regard:

> With no ventilation there will be no rise in temperature, and the zero point (Figure 8) will represent the conditions of coal sealed from the air, or so densely packed that air can not circulate. If there is sufficient ventilation, the heat is all carried away as fast as generated, and some point as at *B* on the zero line will represent this condition as in the case of coarse coal. At some point as at *A* between these two extremes, there may be a condition of ventilation which will supply just oxygen enough to provide for a maximum rise in temperature. What sort of curve represents all of the intermediate conditions between *C*, *A* and *B*, is not known; but that the curve must first ascend and then descend is perfectly evident. This curve teaches that, if we have a condition of ventilation as at *D*, an increase of ventilation at *E* will produce a more favorable condition for a rise in temperature. On the other hand, if the original condition is as at *F*, and the ventilation to *C* is increased, a reduction in temperature can be expected. Since there is no means of knowing just what the ventilation is at any given portion of the pile, there is great hesitancy in advocating ventilating schemes for coal piles, as we are as likely to make trouble as to prevent it, unless extreme and uniform ventilation is assured.

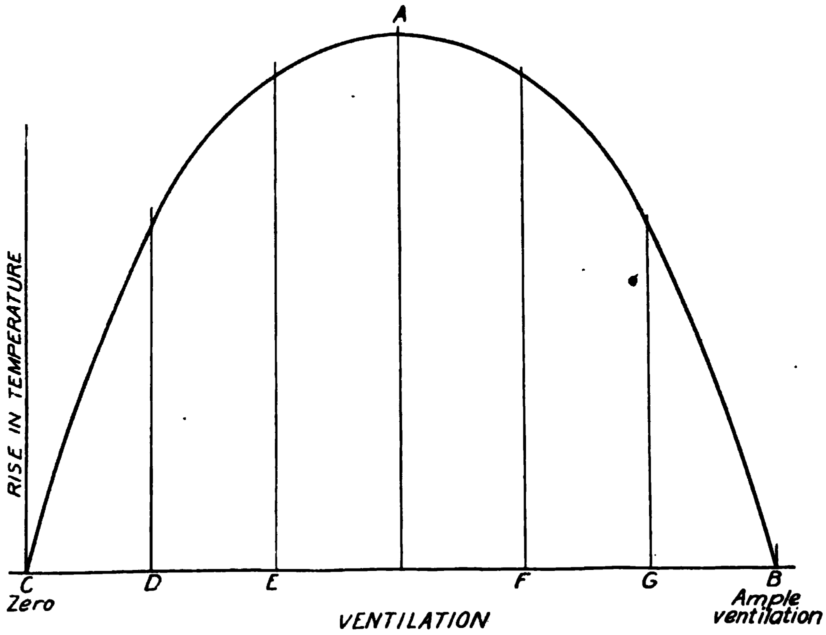

FIGURE 8.—*Relation of heating to ventilation in a portion of a coal pile.*

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[37] Hood, O. P., Factors in the spontaneous combustion of coal, Bureau of Mines Tech. Paper 311, 1922, 9 pp.

Experience has shown that attempts at ventilation only aggravate the heating conditions, doing more harm than good. The majority of owners of coal stocks advocate exposing the coal to a minimum of air, many going so far as to store under water to prevent oxidation of the coal. This is absolute assurance against fines and deterioration, but whether the construction of such elaborate storage devices and the increased cost in handling are warranted, are matters to be decided in individual cases. In this connection it might be stated here that a review of coal-storage practice during 1921, by Stoek[38], will be found worth perusal. Also a description[39] of the under-water storage system employed by the Duquesne Light Company at its great power plant at Brunot's Island along the Ohio river below Pittsburgh, Pa. The concrete storage pit holds 100,000 tons of coal, about 40 days' supply. This company formerly suffered considerable loss through spontaneous combustion, but has now eliminated all that trouble. Several other large underwater storage-plants are referred to in this paper.

If the conductivity of an entire coal pile were known, also the rate of heat generation, it would be a simple mathematical calculation to tell whether or not there was any danger of spontaneous combustion. Unfortunately, numerous complications enter into the problem, such as convection currents, wind pressure, changing barometric pressure, different sizes throughout the pile, scarcity of oxygen in some portions and excess in others, rate of ventilation, increased rate of oxidation at elevated temperatures, and so forth.

As a step in this direction, some experiments were made on the conductivity of coal and the heat lost on exposure to oxygen at elevated temperatures. The conductivity of several sizes of coal was determined in the following manner:

A spherical heater was placed exactly in the center of a spherical flask (figure 9), and the flask filled with sized coal. A thermocouple was placed with one junction at the heater and one in a water-bath in which the flask was placed. Heat was applied at a constant rate until a "steady state" was reached—that is, until the difference in temperature between the center of the coal and the outside of the coal was constant. When this "steady state" was reached, the temperature difference was read on a millivoltmeter. The radii of the spherical heater and of the containing flask were accurately measured by means of a cathetometer, and the rate of

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[38] Stoek, H. H., Coal Industry, vol. 5, Jan. and Feb., 1922, pp. 41 and 103.

[39] Black Diamond, vol. 68, No. 12, 1922, p. 283.

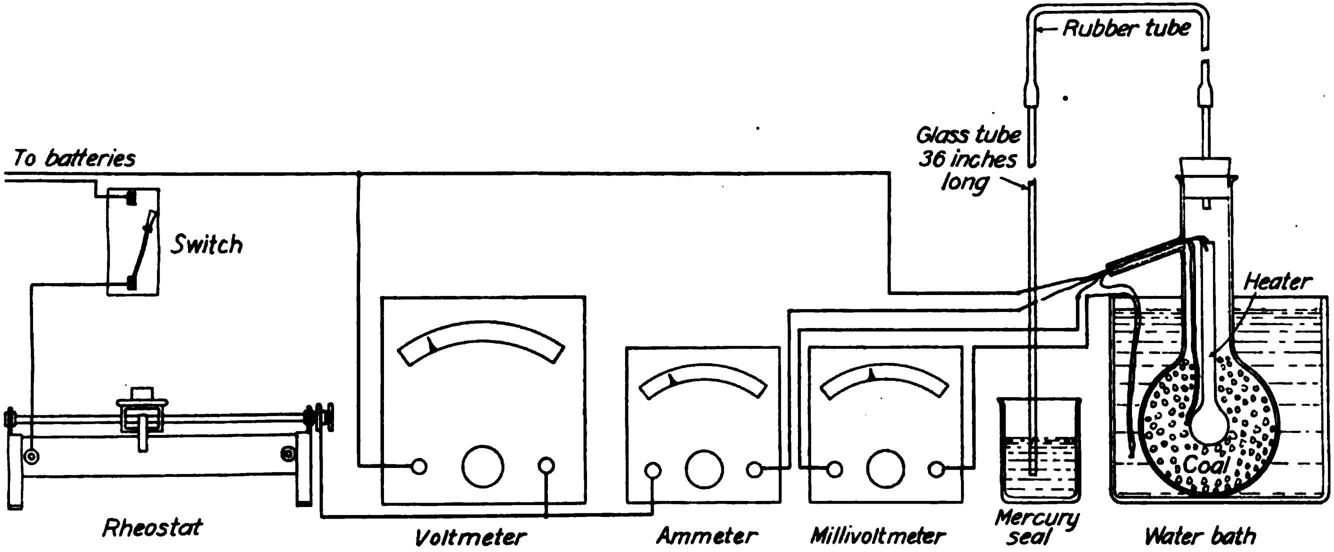

FIGURE 9.—*Apparatus to determine the flow of heat through coal.*

heating was known. Then the total quantity of heat which flowed out in unit time was obtained from the equation[40].

$$\frac{4\pi k\,(\Theta_1-\Theta_2)\,r_1 r_2}{(r_2-r_1)} =$$

calories per second per square centimeter per centimeter thickness, where $(\Theta_1 - \Theta_2)$ is the temperature gradient, in degrees C; and r_1 and r_2 the radii in centimeters of the outer and inner spheres, respectively; and *k* is the heat flow constant.

When *k* is expressed in B. t. u. per hour per square foot per foot thickness per degree F., and *EI* equals watt-hours.

$$\frac{4\pi k\,(\Theta_1-\Theta_2)\,r_1 r_2}{(r_2-r_1)} = \frac{EI}{4.19} \text{ and}$$

$$k = \frac{EI\,(r_2-r_1)}{4.19(4\pi\,(\Theta_1-\Theta_2)\,r_1 r_2)}$$

The following results were obtained from the conductivity tests on Freeport coal:

Size of coal, mesh.	Atmosphere.	E.	I.	$(\Theta_1-\Theta_2)$	K { B. t. u. per hour, per sq. ft., per foot, per °F.
—40 + 60	Oxygen	3.2	0.8	67.6° C.	0.0844
—40 + 60	"	3.2	0.8	69.8	0.0803
—½″ + 3	"	3.2	0.8	54.8	0.1023
—40 + 60	Natural gas	3.2	0.8	64.2	0.0873
—40 + 60	" "	3.2	0.8	65.7	0.0852
—20 + 40	" "	3.2	0.8	49.0	0.114
—½″ + 3	" "	3.2	0.8	53.6	0.1045

The thermal conductivity is not constant, but varies with temperature. In the case of metals, *k* usually decreases with rising temperature, while for most other substances the reverse is true. From the experiments conducted, it is impossible to say how coal conductivity varies, but it appears as though it would increase with the temperature, since the coal is a non-metallic substance. If this is the case, the rate of dissipation of heat would be somewhat more rapid at elevated temperatures, but not sufficient to equalize the increased rate of heat generation.

A wide variation of estimates on the rate at which heat is generated in a coal pile, or the rate of heat loss, have been made. Parr and Wheeler[41] found that Illinois coal—nut size—exposed to weather, suffered a loss of from 5 to 29 B. t. u. per pound per day during the first 7 days; from 3.9 to 4.6 B. t. u. per pound during 60 days; and from 0.3 to 1.3 B. t. u. per pound per day during a year. The screenings from these same coals lost from 17 to 23 B. t. u. per pound per day for the first 7 days, and from 0.6 to 6 B. t. u. per pound per day during one year's open storage.

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[40] Ingersoll, L. R. and Zobel, O. J., Mathematical theory of heat conduction, 1913, p. 27.

[41] Parr, S. W., and Wheeler, W. F., University of Illinois, Eng. Exp. Station Bull. 38, 1909.

Porter and Ovitz[42] found that bituminous coals lose 1 per cent of their calorific value during one year's open storage, 2 per cent in two years, and 3 per cent in five years. Pittsburgh coal, ¾-inch size, stored at Ann Arbor, Michigan, lost only 4 B. t. u. per ton, during six months' storage. Pocahontas coal stored at the Isthmus of Panama lost 14 B. t. u. per pound in three months and 59 B. t. u. per pound in six months. Coal from Sheridan, Wyoming, lost 313 B. t. u. per pound in three months, and 500 B. t. u. per pound in six months. This is a sub-bituminous coal, and would be expected to weather more rapidly than either Pittsburgh, Pocahontas, or New River coal.

To determine the loss in calorific value of coal in an atmosphere of oxygen at slightly elevated temperatures, several experiments were made. The heating value of a sample was accurately determined in an oxygen bomb calorimeter. Then another weighed sample was heated in a sealed tube filled with oxygen in a constant temperature oven. At the expiration of the allotted time, the coal was removed and its calorific value accurately measured. The following results were obtained on different samples:

Coal.	Heating value of fresh coal, cal.	Heating value of oxidized coal, cal.	Heat per hour developed.		Temperature, °C.	Time of heating hours.
			Per lb., B. t. u.	Per cu. ft., B. t. u.		
Freeport (40-60 mesh)	7500	7485	6.7	531	118	4
	8349	8340	....	...	...	..
New River	8346	8340	1.77	139	116	4½
(air dried)	8349	....	....	...	...	..
Pittsburgh coal	7983	7970	7.5	594	80	3
(fresh)	7986	7974	...	...	...	..
	7985	7973	7.8	619	100	3

The loss in heating value of fresh Freeport coal in 4 hours is 0.20 per cent, and for fresh Pittsburgh coal, 0.21 per cent in the same time. New River coal—air dried—loses only 0.096 per cent of its calorific value in 4½ hours.

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[42] Porter, H: C., and Ovitz, F. K., Deterioration in the heating value of coal during storage. Bureau of Mines Bull. 136, 1917, 38 pp.

In fresh Freeport coal (40 to 60 mesh) the heat generated is 6.7 B. t. u. per pound for three hours, as shown above. The specific gravity of the coal was determined as 1.27, and the specific heat is 0.273.

Knowing the rate of generation of heat per unit of coal and the rate of heat dissipation, it is possible to solve by Fourier's method the problem of the rate at which any given pile of coal will heat, provided that sufficient air is supplied for oxidation and the effect of ventilation is known. An approximate idea, however, may be gained of the relation of heat generation to heat dissipation from the following considerations:

For example: consider a cubic foot of 40-60 mesh Freeport coal surrounded by an envelope one foot in thickness reacting with just sufficient oxygen to maintain the maximum rate of heat generation. This would be 6.7 B. t. u. per pound or 531 B. t. u. for the cubic foot (79.3 lb. x 6.7). Now the rate of dissipation of heat through the coal is 0.0803 B. t. u. per square foot per foot per 1° F. At 118° C. there would be a temperature gradient between the central block of coal and the outside atmosphere of, say 118° — 25° = 93° C., or 167° F. This times 0.0803 equals 13.4 B. t. u. dissipated per square foot of surface exposed, and the heat travels at equal rates through the 6 faces of the cube considered. The heat dissipated through the envelope would then be roughly 6 times 13.4 or 80 B. t. u. per hour. As opposed to this, heat is generated in the cubic foot of coal at the rate of 6.7 x 79.3, or 531 B. t. u. per hour. A rigid solution of the problem would involve consideration of a differential cube, and solution by the Fourier equation:

$$\frac{\Delta \Theta}{\Delta t} = h^2 \left[\frac{\Delta^2 \Theta}{dx^2} + \frac{\Delta^2 \Theta}{dy^2} + \frac{\Delta^2 \Theta}{dz^2} \right]$$

But this even would not take into consideration the ventilation factor. The above is sufficient to show, however, that at 118° C. it is possible to have conditions that heat will be generated 6.6 times as fast as it is dissipated. Further, in the above case the coal envelope, one foot in thickness was assumed to generate no heat, which obviously would not be true. Any heat generated in the envelope would oppose dissipation and hence increase the heating of the central unit.

The difference between the heat generated and the heat dissipated, or 451 B. t. u.'s, represents the heat retained by the coal. This is sufficient to raise the temperature of a cubic foot of coal about 21° F., or 11.7° C. Even if the rate of generation did not increase rapidly with increased temperatures, a cubic foot of coal with initial temperature of 118° C. under the conditions assumed would ignite spontaneously in 12 hours. However, investigators have said that the rate of heat generation doubles with every increase of temperature of 20°. If this is the case, coal under these conditions would fire in less than six hours. Of course, with larger sizes and with lower initial temperatures, the time would be longer.

It is evident from the low conductivity of coal that a hot spot in the center of a coal pile could exist for some time before there would be any indication of spontaneous heating on the surface.

The above figures all neglect the cooling effect of convection currents. In all probability the maximum cooling effect comes from these rather than from conduction and radiation. On account of varying barometric pressures and differential temperatures throughout the pile, there is a total exchange of air of perhaps 20 to 30 times weekly in a coal heap. If there is a high wind pressure, the change is even greater. Hence the rate of heat dissipation must be much greater than that shown by the conductivity figures alone.

CONCLUSIONS.

As a result of the present investigation and a review of previous opinions, the following conclusions are reached:

1. As demonstrated in the experiments —200 mesh coal has a critical temperature of 171° C., while — 10 + 20 mesh coal has a critical temperature of 231° C. Coal coarser than ¼ inch showed no rapid self-heating throughout the range of the experiments. The reason for this is apparent when we consider that the rate of oxidation is dependent on the surface exposed, and that —200 mesh coal has over 18 times as much surface as an equal weight of —20 + 40 mesh coal. Therefore the presence of fines in a coal pile should be avoided. Coal should be handled as little as possible and should be screened, wherever practicable, before storing.

2. The experiments show that with the same coal, moist air will give a lower critical temperature than dry air. This is in accordance with the conclusions of previous investigations which showed that the presence of moisture in the air or in the coal itself facilitates oxidation and consequent heating. Wetting the coal pile to retard heating is not good practice unless the coal is completely immersed.

3. Artificial mixtures of coal and pyrite in various proportions showed a critical temperature no lower than that of the coal

alone, while pure pyrites had a critical temperature 26° C. higher than the coal. From this it appears that massive pyrite or "brass lumps" are not dangerous in a coal pile. Iron sulphide finely disseminated in microscopic nodules may be a subsidiary cause of heating, but to just what extent is not known. The distinction between the action of pyrite and marcasite has not been definitely established, nor have the microscopic nodules been identified absolutely as marcasite or pyrite. This point would merit further investigation.

4. Mixtures of fresh coal with coal partly oxidized showed a critical temperature of 174° C., as compared with 168° C. for the fresh coal alone. Instead of hastening spontaneous combustion, partly oxidized coal seems to act as a deterrent when mixed with fresh coal. It appears that the danger in mixing two grades of coal, or in storing coal on the same pile at different times, arises from physical rather than chemical causes. If no heating has occurred at the surface of the heap, it is safe to pile more coal on top, provided there is no accumulation of fines at the contact of the new and old coal. A mixture of two kinds of coal will heat more rapidly than the poorer of the two.

5. The coal constituents as recognized under the microscope show a difference in critical temperature,—that of anthraxylon being at 172° C., and that of attritus at 198° C. However, contrary to what would be expected, coals in which anthraxylon predominates do not have lower critical temperatures. The coal constituents undoubtedly have a bearing on spontaneous combustion, but the exact function of each is a problem to be solved.

6. The rate of heat generation at slightly elevated temperatures is very rapid as compared to the dissipation due to the low conductivity of the coal. In large piles, much of the heat generated is retained by the coal and accumulates until a dangerously high temperature is reached. Assuming that the heat is dissipated by conduction alone, —40 + 60 mesh Freeport coal with an initial temperature of 118° C. would fire in less than six hours. Fortunately, however, considerable heat is dissipated by convection currents. On account of the low conductivity of coal, cooling by artificial ventilation is almost impossible unless the air reaches every part of the pile. Generally the air travels through the stack in currents, and exerts no cooling effects on parts a short distance away from its channels. Exclusion of air as much as possible, in order to stop oxidation, is more successful than attempts at ventilation to dissipate the heat generated.

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CRAMER PTG. & PUB. CO.,
CRAFTON, PA.

Bulletin 4

COAL-MINING INVESTIGATIONS

UNDER AUSPICES OF

CARNEGIE INSTITUTE OF TECHNOLOGY,
UNITED STATES BUREAU OF MINES,
ADVISORY BOARD OF COAL-MINE OPERATORS
AND ENGINEERS.

CORROSION TESTS ON METALS AND ALLOYS IN ACID MINE WATERS FROM COAL MINES.

By

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and

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CARNEGIE INSTITUTE OF TECHNOLOGY,
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PREFACE.

Pittsburgh is the greatest industrial center in America, and the heart of the greatest bituminous coal-mining district in the world. It is eminently desirable, therefore, that this city should have an institution which devotes a part of its great facilities to the scientific study of that branch of the industry which is largely responsible for Pittsburgh's development and that of western Pennsylvania.

On May 27, 1919, a number of the leading representatives of the coal-mining industry of western Pennsylvania met in conference with the then President of the Carnegie Institute of Technology with a view of bringing about closer relations between the Institute and the mining interests. It was felt that the advice and cooperation of men in the field were necessary for the training of young men for mining work, and at the conclusion of the meeting the following resolution was adopted:

> That this gathering give its approval and moral and material support to the form of education proposed for the Carnegie Institute of Technology by which students may receive a combined technical, practical, and business training, necessary to fit them for service in the coal mining and allied industries. Further, that the President of the Carnegie Institute of Technology appoint a board of no less than ten men representing the coal mining and allied industries, the United States Bureau of Mines, the State Department of Mines, and the Carnegie Institute of Technology, who will advise and assist in carrying out this program of education and training, particularly in its practical phases to the mining industry and in its cooperation with the United States Bureau of Mines.

Following further the intention of this resolution, the President of the Institute entered into a cooperative agreement on June 1, 1919, with the Director of the United States Bureau of Mines whereby full advantage could be taken of the Bureau's laboratories, equipment, and library, as well as of the advice and instruction of its technical staff.

To carry out this new program there was organized during the summer months the Cooperative Mining Courses in the Department of Mining and Metallurgical Engineering, College of Engineering, of the Institute. The course in mining engineering covers four years, and leads to the degree of Bachelor of Science. The two-year course in coal mining is planned to prepare men with a certain amount of practical experience for executive positions. The four-weeks intensive summer course in coal mining is designed for miners who aspire to be firebosses and mine foremen. In a large measure, the new mining, ore-dressing, and coal-washing laboratories at the Institute have been equipped gratuitiously by various manufacturers of mining machinery and appliances. Cooperative research through teaching and research fellowships is devoted to various problems in coal mining and the utilization of fuels. The Institute selects the fellows; the Bureau of Mines provides the laboratory facilities; and the Advisory Board determines what problems be undertaken, and publishes the reports.

The primary object of this cooperation of the Carnegie Institute of Technology, the United States Bureau of Mines, and the Advisory Board of Coal-Mine Operators and Engineers, is the proper education and training of young men for the mining industry. The ultimate objective is to bring about better conditions and greater efficiency in mining operations. The decrease in reserves of coal and increasing cost of production make it urgently necessary for mine operators and engineers to take advantage of everything which modern science, machinery, and methods can contribute.

EDWARD STEIDLE,
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FOREWORD.

The investigation described in this paper was conducted by the Cooperative Mining Courses of the Department of Mining of the Carnegie Institute of Technology and the Pittsburgh Experiment Station of the U. S. Bureau of Mines in cooperation with the coal-mining industry of western Pennsylvania. Under cooperative agreement, four research fellowships paying $750 per annum per year of 10 months are supported by the Carnegie Institute. These fellowships are open to properly qualified graduates of universities and technical schools. The research work is carried on in the laboratories of the Bureau of Mines under the direction of a member of the Bureau research staff, and is published under the joint authorship of the two investigators.

Fellowship holders are required to register at the Institute as graduate students and become candidates for the degree of Master of Science, unless an equivalent degree has been previously earned. The purpose of these fellowships is the solution of problems in mining and utilization of coal.

The corrosion tests on metals and alloys in acid mine water from coal mines was undertaken at the suggestion of the Advisory Board of coal operators with a view of obtaining information as to the acid-resisting properties of the various metals and alloys available for use in underground equipment exposed to the corrosive action of acid mine waters. The tests showed that most of the alloys available for use in coal mine equipment were corroded extensively by the acid waters. Brasses, which contain considerable zinc, were corroded rapidly; bronzes containing considerable tin were also corroded, but to a less extent than the brasses; cupro-nickel and nickel-silver alloys were corroded about to the same extent as the brasses. Alloys that were practically unattacked by the acid mine waters include a high chromium steel, two highly alloyed chromium-nickel-silicon steels, a nickel-chromium-iron alloy, and a high-silicon cast iron. These resistant materials possess certain disadvantages for general use in coal mine equipment, such as the brittleness and hardness of the high-silicon cast iron and the relatively high cost of the others. However, these resistant materials should prove satisfactory for use in such pump parts and other equipment where these factors are not a serious consideration.

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The cooperation of the officials of the H. C. Frick Coke Co., the Hillman Coal & Coke Co., and the Pittsburgh Coal Co., at whose mines the tests were made, is gratefully acknowledged. The local employees of the mines rendered valuable assistance in installing the equipment for the tests.

Acknowledgment is made to the following companies who kindly cooperated by supplying test specimens of metals and alloys:

The Ajax Metal Co.
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The American Rolling Mill Co.
The Aterite Company.
Bethlehem Foundry and Machine Co.
Bridgeport Brass Co.
Bronze Die Casting Co.
The Cleveland Brass Manufacturing Co.
Crane Company of Chicago.
Crucible Steel Company of America.
Driver-Harris Company.
The Duriron Company, Inc.
Hendricks Brothers, Inc.
Ingersoll-Rand Company.
The International Nickel Co.
Lumen Bearing Co.
Midwest Engine Co.
Rich Tool Co.
Scoville Manufacturing Co.
Union Carbide and Carbon Research Laboratories, Inc.
Waukesha Foundry Co.
The William Cramp Sons Ship & Engine Building Co.

CORROSION TESTS ON METALS AND ALLOYS IN ACID MINE WATERS FROM COAL MINES.

By W. A. SELVIG *and* GEORGE M. ENOS.

INTRODUCTION.

Water from coal mines is usually decidedly acid in character, and causes considerable trouble and expense owing to its corrosive action on mine equipment. Little information is available concerning the corrosive action of acid mine water on the various metals and alloys available for use in underground equipment, so such data should be of value to manufacturers and users of mine pumps and other equipment exposed to the action of such water.

The corrosion test described in this paper is a comparative corrosion test on 45 different metals and alloys. Three test specimens of each metal and alloy were completely immersed in flowing water at each of three coal mines in the western Pennsylvania coal region. The waters from these mines covered a wide range of acidity, from one considered to be below the average of that region to a water which is considered to be extremely acid.

Inspections were made at regular intervals, and the degree and nature of corrosion was noted. At the completion of the test, the specimens were removed, cleaned, and the extent and nature of the corrosion recorded. Samples of the mine waters were collected at each inspection, and the degree of acidity determined. Complete analyses were also made on the waters from the three mines.

HISTORY AND SCOPE OF PREVIOUS INVESTIGATIONS.

Although it is a well-known fact that water from coal mines is frequently extremely acid, little attention has been paid to the comparative corrosion of metals and alloys in mine water. Water from metal mines is also frequently corrosive in its action, as at the copper mines in the Butte district. Neutralization of mine water has been attempted in many cases, notably on the Rand in South Africa, and at several mines in western Pennsylvania. As it is impractical to neutralize the water underground, the problem of the corrosion of pump parts, pipes, and similar equipment is not solved by neutralizing the water after pumping to the surface. In many cases, however, neutralization, followed by settling and filtering, will provide water suitable for use in boilers.

Until recently, little research has been done on the fabrication of alloys for resisting the action of acid mine water. Many alloys or materials which resist atmospheric or sea water corrosion are not at all suitable for use in mining equipment which will be subjected to the action of acid mine water.

Space does not permit of the review of the extensive literature on corrosion in general, and only work that has a direct bearing on the corrosive action of mine water and the resistance offered by metals and alloys to such action, will be reviewed in these pages.

While working with water from the Monongahela River in the vicinity of Pittsburgh, Pa., which is decidedly acid at times, Clement and Walker[1] found that it was possible to prevent corrosion of iron immersed in dilute solutions of sulphuric acid by imposing a counter electromotive force. They also found that the density of current required to prevent corrosion depends on various factors, the more important being concentration of the acid, amount of dissolved oxygen, and rate of circulation of the solution.

From a study of these factors in their experiments they found the current density necessary to prevent corrosion under various conditions. Knowing the loss in weight of the unprotected metal under given conditions, it was possible to calculate the current density required.

No application of these principles in practical work in preventing corrosion by mine water or acid river water has been noted in the literature. Obviously, further experiment with large scale apparatus would be necessary in order to verify the practicability of this method of preventing corrosion. It would seem simpler to use materials in pump parts, pipe-lines, and other equipment, which would not be corroded by the water, provided such materials are available, can be easily fabricated, and are reasonable in price.

Clark and Ilsley[2] tested insulating materials used on electric conductors, imitating conditions found in mines as nearly as possible. They concluded that the deleterious substances in the various mine waters examined were mainly sulphuric acid and iron sulphates. They made up synthetic mine waters, somewhat stronger than the most acid water of which they had record, and a preliminary series of tests were made on insulating materials.

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[1] Clement, J. K., and Walker, L. V., An electrolytic method of preventing corrosion of iron and steel: Bureau of Mines Tech. Paper 15, 1913, 19 pp.

[2] Clark, H. H., and Ilsley, L. C., The action of acid mine water on the insulation of electric conductors: Bureau of Mines Tech. Paper 58, 1913, 26 pp.

It is pointed out by Friend[3] that the rate of solution of a metal in an acid is not a measure of the resistance to corrosion which the metal would offer in a neutral medium. He also found that some steels corrode more rapidly in dilute sulphuric acid than do others. In 7.5 per cent sulphuric acid, "acid" steel had a corrosion factor 3 times as great as "basic" steel.

Watts[4] studied the effect of adding various substances to dilute solutions of sulphuric acid in corroding test specimens of iron, and he attributes the retardation of corrosion when salts of arsenic, tin, chromium, and mercury are used to their high over-voltage. Metals of low over-voltage, which deposit on iron from solution, such as copper, are, in general, accelerators of corrosion.

Blakely[5] discusses the nature of mine water from anthracite coal mines, and states that the waters vary in composition, some even being alkaline, though they are generally acid. An unusually acid water had a free acidity of 14,700 parts per million, and 156,800 parts per million total acidity. The following are typical analyses of acid waters from anthracite mines:

Typical analyses of acid mine waters from anthracite coal mines.

(Parts per million of H_2SO_4).

Sample No.	6	7	8	9	10
Appearance	Turbid yellow	Clear yellow	Clear	Yellow	Yellow
Free H_2SO_4	398	412	701	98	622
Total acidity calculated as H_2SO_4	397	706	1205	1824	3725
Oxides of iron and aluminum (Fe_2O_3 and Al_2O_3)	158	366	831	913	1676
CaO	391	163	127	116	489
MgO	174	62	24	168	631
SO_3	1222	1122	1567	1915	6037
SiO_2	32	41	52	Not determined	
Organic and volatile matter	457	795	1295	Not determined	
Total solids	2419	2189	3421	4100	10083

Blakely also states that it is usually best to use wood-lined pipes for conducting mine water.

In discussing the chemistry of mine water, Young[6] notes the manner in which mine water may reach the coal seam, and the geological conditions affecting the method of flow and the composition of the water. The source of the sulphuric acid is the oxidation of the pyrite present, and the chemical reactions involved are rather complex. He also discusses the corrosive action of the water, and gives illustrations of how it attacks concrete.

---

[3] Friend, J. Newton, The relative corrodibilities of iron and steel: Trans. of Faraday Soc., vol. XI, April, 1916, p. 204.

[4] Watts, O. P., The effect of various substances on the rate of corrosion of iron by sulphuric acid: Trans. of Amer. Electrochem. Soc., vol. XXI, 1912, p. 237.

[5] Blakely, A. G., Chemistry in coal mining: Coal Age, vol. 10, No. 8, Aug. 19, 1916 p. 296.

[6] Young, C. M., The chemistry of mine water: Coal Age, vol. 10, No. 18, Oct. 28, 1916, p. 705.

In non-oxidizing acids, such as normal sulphuric, Richardson[7] states that relatively pure iron dissolves at a low rate, while less pure iron, such as cast iron, dissolves at a relatively high rate. In the case of normal nitric acid, the opposite results are noted. In this case the results obtained with sulphuric acid are not comparable to mine water, as ferrous and ferric sulphates are usually present in mine water.

Committee A-5, on Corrosion of Iron and Steel, of the American Society for Testing Materials, through its sub-committee[8] on total immersion tests, conducted a comprehensive mine water corrosion test on a large number of irons and steels of varying composition. The test specimens were 2 by 6 inches in size, and represented both 16 and 22-gage material. The test was made by immersing the test specimens in flowing acid mine water at the Calumet coal mine of the H. C. Frick Coke Co., at Calumet, Pa. The test specimens were considered to have failed if they had been corroded through or eaten away at the edge for a distance of ¼ inch. After failure, the specimens were cleaned, weighed, and the corrosion loss calculated. Photographs of the corroded test specimens were also made.

The action of the acid mine water on all of the test specimens was severe, and it is evident from the tests that the ordinary grades of iron and steel are corroded rapidly by acid water from coal mines. Copper-bearing steels, which proved to be very resistant to atmospheric corrosion, were corroded rapidly by the mine water.

In connection with the tests made at the Calumet mine it was found necessary to study the nature of acid water from coal mines, and to modify the standard methods of water analysis to meet the conditions existing in mine water. Selvig and Ratliff[9] found that titration of acid mine water for free sulphuric acid with standard alkali solutions gave too high results, due to hydrolysis of sulphates of iron and aluminum. More nearly correct results were obtained by reducing the ferric sulphate present to ferrous sulphate, prior to titration. This reduction was effected by the addition of potassium iodide solution to the mine water.

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[7] Richardson, W. D., Rate of solution of iron and steel in non-oxidizing and oxidizing acids: Twelfth semi-annual meeting of the Am. Inst. of Chem. Eng., 1920.

[8] Report of Sub-Committee 5 on Total immersion tests, Proc. Amer. Soc. Test Materials, vol. 21, 1921, pp. 157-194.

[9] Selvig, W. A., and Ratliff, W. C., The nature of acid water from coal mines and the determination of acidity: Jour. Ind. and Eng. Chem., vol. 14, No. 2, p. 125.

Corrosion by acid water from coal may occur in other places than in the mines. Jackson[10] notes that a cable-sheath had been corroded and the cable broken down, owing to acid water draining from an adjacent coal pile.

NATURE OF CORROSION.

It is beyond the scope of this paper to discuss the various theories regarding the mechanism of corrosion which have been advanced at different times. Cushman and Gardner[11] have presented these theories in connection with work done on the corrosion of iron and steel, to which the reader is referred. The literature on corrosion is extensive, and a complete bibliography on metal corrosion and protection up to 1915 has been compiled by the Carnegie Library of Pittsburgh[12].

The electrolytic theory of corrosion is most generally accepted at the present time. This theory assumes that a metal in contact with water tends to dissolve owing to a tendency of the metal to pass from an atomic to an ionic state. Water is dissociated to a small extent into positively charged hydrogen ions ($\overset{+}{H}$) and negatively charged hydroxyl ions ($\overset{-}{OH}$). Under these conditions the metal tends to replace the positively charged hydrogen ions in the solution. The addition of acid to water causes a marked increase in concentration of hydrogen ions present, consequently solution of the metal proceeds at a more rapid rate.

Impervious surface coatings, may, under certain conditions, form on the metal, and protect the underlying metal from further corrosion, or at least greatly retard corrosion. Aluminum and copper, for example, oxidize rapidly in air and form superficial coatings which tend to prevent further corrosion. On the other hand, porous coatings may form which do not protect the underlying metal; and in some instances the corrosion may be accelerated owing to a difference of potential between the metal and the coating. Iron, for example, corrodes more rapidly in air after the formation of appreciable amounts of rust, the accelerated corrosion being due to a difference in potential between the iron and the rust.

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[10] Jackson, R. H., Corrosion caused by coal pile seepage: Power, vol. 50, No. 18, 1919, p. 671.

[11] Cushman, A. S., and Gardner, H. A., The corrosion and preservation of iron and steel: 1910, 373 pp; McGraw-Hill Book Co., New York City.

[12] Metal corrosion and protection, Carnegie Library, Pittsburgh, Pa., Monthly Bulletin, July, 1909: Metal corrosion and protection (supplement), Proc. Eng. Soc. West. Pa., vol. 31, 1915, pp. 193-222.

From a theoretical consideration it is evident that a great deal of research remains to be done in order to arrive at an intelligent understanding of corrosion of metals and alloys under varying conditions. So many factors are involved, which are not well understood, that practical corrosion tests should be made under conditions as comparable as possible to those under which the material is to be used.

NATURE OF ACID WATER FROM COAL MINES.

Water from coal mines is usually decidedly acid, containing free sulphuric acid, and ferrous, ferric, and aluminum sulphates, in addition to sulphates of calcium, magnesium, sodium, and potassium, together with silica, and usually some chlorides. On standing, dilution, aeration, or warming, insoluble iron compounds tend to precipitate, principally as hydrous ferric oxides.

The occurrence of iron sulphates and free sulphuric acid is due to the action of water and air on the pyrite or marcasite associated with the coal. These substances are oxidized to ferrous sulphate, ferric sulphate, and sulphuric acid; the reactions may be represented as follows:

$$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4$$
$$4FeSO_4 + 2H_2SO_4 + O_2 = 2Fe_2(SO_4)_3 + 2H_2O.$$

In connection with experimental work[18] conducted by the Bureau of Mines, a number of mine waters were collected and analyzed, and it was found that the acidity and composition varied considerably at different times. The analyses of these waters is given in table 1 to give a general idea of the composition of such waters:

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[18] Clark, H. H., and Ilsley, L. C., Action of acid mine water on the insulation of electric conductors: Bureau of Mines Tech. Paper 58, 1913, 26 pp.

TABLE 1.—*Analyses of some mine waters collected at various coal mines.*

(Parts per million[a])

Laboratory No.	Silica. (SiO_2)	Ferrous iron. (Fe^{++})	Ferric iron. (Fe^{+++})	Aluminum. (Al)	Calcium. (Ca)	Magnesium. (Mg)	Sodium. (Na)	Chlorine. (Cl)	Total sulphate radical. (SO_4)	Free sulphuric acid. (H_2SO_4)
10848	36	967	145	60	436	196	85	18	4755	442
10966	40	220	884[b]	[b]	162	77	75	25	6370	3662
11785	26	89	299	63	204	130	27	2	2374	93
11786	22	17	12	...	267	112	100	6	1406	106
11787	16	44	157	25	291	168	65	6	2234	185
11788	32	6	56	...	234	110	133	Trace	1562	203
11789	20	3	51	...	79	34	97	Trace	790	248
11790	29	Trace	11	...	232	118	66	7	1296	88
11791	48	11	915	148	800	197	54	2	4370	Trace
19825	64	6	320	111	295	79	21	...	2764	277

[a] *To convert parts per million to grains per U. S. gallon, multiply by 0.0583.*

[b] *Ferric rion and aluminum in this sample were not determined separately—884 represents ferric iron as ferric oxide (Fe_2O_3) plus aluminum oxide (Al_2O_3).*

METHOD OF MAKING CORROSION TESTS.

Field versus laboratory tests.—As the various factors effecting corrosion are apparently numerous and not definitely understood, it was considered best to make the tests in actual mine water rather than in synthetic water. Mine water is also of such complex composition that it would be difficult to prepare synthetic waters in sufficiently large quantities to permit making corrosion tests on a large number of test specimens over an extended period of time. It would also be difficult to prepare apparatus to circulate the water so as to maintain a continuous uniform flow of water around the test specimens. The tests were therefore made at the mines where an unlimited amount of water was available, and the test specimens could be subjected to the same conditions.

Preparation of test specimens for corrosion tests.—The different metals and alloys were in the form of rectangular pieces 2 by 6 inches in size, the rolled materials being approximately 16 gage (B and S) thick (0.051 inch), and the cast materials approximately ¼ inch thick. The test specimens were carefully surfaced by machining, grinding, or polishing with fine emery cloth to remove all surface products formed during their fabrication. All cast specimens were surfaced by machining, except two high-silica irons which required grinding on account of their hardness. All specimens of rolled material were surfaced by polishing with fine emery cloth. After surfacing, the specimens were carefully measured and weighed.

Design and installation of test-boxes.—The test-boxes for making the corrosion test were designed to permit total immersion of the test specimens in flowing water. The boxes and racks for holding the specimens were made of wood. A system of four baffles was built in the boxes so as to obtain a uniform flow of water around each specimen. The construction of the test-boxes and racks is shown in figure 1. The slots for holding the test specimens in the racks were cut so as to allow ¾ inch spacing between the faces of the specimens.

Apparatus was installed at three coal mines—namely, the Montour No. 1 mine of the Pittsburgh Coal Co., at Southview, Washington County, Pa.; the Edna No. 2 mine of the Hillman Coal & Coke Co., at Wendel, Westmoreland County, Pa.; and the Calumet mine of the H. C. Frick Coke Co., at Calumet, Westmoreland County, Pa.

At the Montour No. 1 mine a sufficient head of water could not be obtained to cause a continuous flow of water through the test-boxes, so the racks containing the test specimens were placed

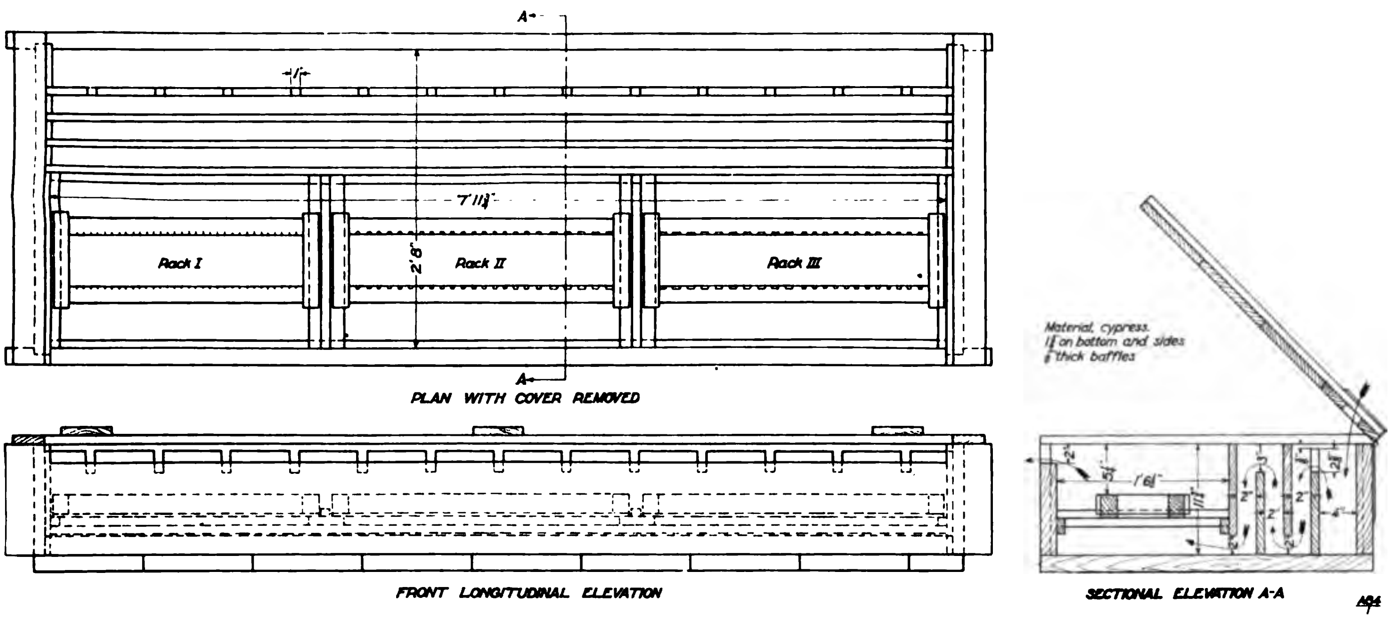

FIGURE 1.—*Construction of wooden test-boxes.*

directly in the mine sump. The specimens were totally immersed in the mine water and subjected to a gentle flow of water. Copper-bearing and non-copper-bearing materials were placed in separate racks.

The test-boxes were installed at both the Edna No. 2 and Calumet mines. The copper-bearing and non-copper-bearing materials were placed in separate boxes. At the Edna No. 2 mine the installation was placed underground. A wooden box, acting as a reservoir, was placed above the boxes, and the water conducted to the boxes by means of rubber hose. The rate of water flow was so regulated as to change the water content of each box once in every 15 minutes. Under these conditions the velocity of water flow around the test specimens was 1.8 inches per minute. This rate was kept constant throughout the test and was obtained by inserting a wooden plug, with circular orifice, into the rubber hose. The boxes were carefully levelled so that the overflow would be uniform over the entire length of the box, thus subjecting all test specimens to the same velocity of water flow.

Plate I.—*Arrangement of test-boxes for mine water corrosion tests at Calumet mine.*

At the Calumet mine the installation was similar to that at the Edna No. 2 mine, except that the test-boxes were placed above ground. It was not necessary to use a water reservoir as the water from the mine was pumped by wooden-lined pumps through wooden-lined pipes into wooden-lined concrete towers. One of these towers acted as a standpipe in maintaining a constant head of water. The rate of flow was regulated so as to be the same as at the Edna No. 2 mine—the flow through the boxes being so regulated as to give a velocity of 1.8 inches per minute around the test specimens. The arrangement of the boxes at the Calumet mine is shown on Plate 1.

Inspection of tests.—Inspections were made at each mine at intervals of one or two weeks, depending on the apparent rate of corrosion at the three mines. At each inspection, each test specimen was removed and the nature and extent of corrosion noted. The specimens were rinsed in water, and any corrosion products which could be rubbed off with the hand were removed. The temperature of the water in the test-boxes was taken, and samples of water were collected for determination of acidity.

Test specimens that had been corroded through or corroded away at the edge for a distance of about ¼ inch were considered to have failed, and were removed. Also, specimens were removed if they had corroded uniformly thin so that they might fall out of the racks before the next inspection.

The test covered a period of 119 days at the Montour No. 1 mine, 135 days at the Edna No. 2 mine, and 98 days at the Calumet mine.

WATER ANALYSES.

Acidity determinations.—The samples of water collected at each inspection were titrated for acidity not later than the day following collection. Acidity due to free sulphuric acid, and acidity due to free sulphuric acid plus sulphates of iron and aluminum, was determined by titration with standard sodium carbonate solution. Work done by the Bureau of Mines[14] indicates that acidity due to free sulphuric acid in the presence of ferric sulphate can be determined fairly satisfactorily by direct titration with alkali solutions in the presence of methyl orange, after reduction of the ferric sulphate to ferrous sulphate previous to titration. The free acidity thus determined will, however, be somewhat too high, due to hydrolysis of aluminum sulphate. The method consists of adding a slight excess of potassium iodide solution to the water, and subsequently converting the liberated iodine formed to sodium iodide by the addition of a slight excess of sodium thiosulphate solution, measured by the disappearance of the yellow color caused by the free iodine. The reactions are as follows:

$$Fe_2\,(SO_4)_3 + 2KI = K_2SO_4 + 2\,FeSO_4 + 2I$$
$$2I + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6.$$

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[14] Selvig, W. A., and Ratliff, W. C., The nature of acid water from coal mines and the determination of acidity: Jour. of Ind. Eng. Chem., vol. 14, No. 2, Feb., 1922, p. 125.

Total acidity, due to free sulphuric acid plus sulphates of iron and aluminum, was determined by titrating boiling dilute portions of the mine water with standard alkali solution in the presence of phenolphthalein as an indicator. The dates of collection, acidity due to free sulphuric acid, total acidity due to free sulphuric acid plus sulphates of iron and aluminum, and water temperatures at the time of collection are given in table 2. As will be noted from the table, the water from the Calumet mine was the least acid of the three mines. The water from the Montour No. 1 and Edna No. 2 mines was extremely acid—the latter having the highest acidity during most of the period covered by the test.

Complete analyses of mine waters.—Two samples of water from each mine were collected during the period of the test, and complete mineral analyses were made on the filtered water, the results of these analyses are given in table 3. It will be noted that the water from the Montour No. 1 mine was high in chlorides.

TABLE 2.—*Acidity (parts per million in terms of sulphuric acid) and temperature of mine waters during test.*

Montour No. 1 mine.				Edna No. 2 mine.				Calumet mine.			
Date.	Water temperature, °C.	Acidity due to free sulphuric acid, p. p. m.	Acidity due to free sulphuric acid plus sulphates of iron and aluminum, p. p. m.	Date.	Water temperature, °C.	Acidity due to free sulphuric acid, p. p. m.	Acidity due to free sulphuric acid plus sulphates of iron and aluminum, p. p. m.	Date.	Water temperature, °C.	Acidity due to free sulphuric acid, p. p. m.	Acidity due to free sulphuric acid plus sulphates of iron and aluminum, p. p. m.
Dec. 5, 1921...	....	2000	10300	Nov. 15, 1921...	....	3100	13250	Dec. 20, 1921...	....	520	3710
Dec. 12, 1921...	16.5	1410	11310	Nov. 22, 1921...	15.0	2950	12970	Jan. 5, 1922...	15.0	500	3200
Dec. 19, 1921...	16.5	1550	11280	Dec. 6, 1921...	14.0	2570	11690	Jan. 19, 1922...	15.0	660	3330
Jan. 2, 1922...	16.5	2480	18160	Dec. 13, 1921...	15.0	2860	15650	Feb. 2, 1922...	12.8	340	2950
Jan. 16, 1922...	16.5	1810	10780	Dec. 20, 1921...	14.5	3200	16400	Feb. 16, 1922...	14.2	270	2990
Jan. 31, 1922...	16.3	1200	11070	Jan. 5, 1922...	14.0	2110	15850	Mar. 2, 1922...	14.8	480	2820
Feb. 13, 1922...	16.0	1030	11470	Jan. 19, 1922...	14.0	3140	17200	Mar. 16, 1922...	14.6	390	2380
Mar. 6, 1922...	15.9	980	10630	Jan. 26, 1922...	12.8	1940	13280	Mar. 30, 1922...	14.8	270	2180
Mar. 20, 1922...	16.0	1030	9730	Feb. 2, 1922...	....	1100	15390				
April 3, 1922...	15.8	830	8870	Feb. 16, 1922...	13.5	1540	15480				
				Mar. 2, 1922...	14.2	1250	12750				
				Mar. 16, 1922...	16.5	1150	11270				
				Mar. 30, 1922...	16.5	1150	12860				

TABLE 3.—*Analyses of filtered mine waters.*

Constituent.	Montour No. 1 mine.		Edna No. 2 mine.		Calumet mine.	
	Sample No. 1 collected January 31, 1922.	Sample No. 2 collected March 20, 1922.	Sample No. 1 collected January 26, 1922.	Sample No. 2 collected March 16, 1922.	Sample No. 1 collected February 2, 1922.	Sample No. 2 collected March 16, 1922.
	P.p.m.[a]	P.p.m.	P.p.m.	P.p.m.	P.p.m.	P.p.m.
SiO_2	160	155	129	150	67	63
Fe^{++}	1216	1137	516	376	11	104
Fe^{+++}	56	60	1303	413	213	58
Al	1434	1217	1225	1338	236	289
Ca	415	350	307	287	164	210
Mg	9	56	122	174	191	33
K	373	173	332	185	0	131
Na	1816	2286	512	137	61	117
Cl	590	625	37	19	17	13
SO_4	11898	12115	11750	9339	2229	2368
Suspended matter (on unfiltered water) dried at 105° C.	26	13	19	6	43	91

[a] *To convert parts per million to grains per U. S. gallon, multiply by 0.0583.*

AFTER TREATMENT OF THE TEST PIECES.

Test specimens that had failed during the test, and all specimens that remained throughout the test, were given the same treatment after removal from the mine water. They were carefully washed in warm water, and rubbed with a fiber brush to remove loose surface coatings. Following this treatment, the specimens were allowed to stand for 24 hours in tap water, then rinsed with distilled water, dried in an air-oven at 105° C., and carefully weighed. It was thought advisable to soak the pieces in water in order to remove any water-soluble salts which might be present. The chemical composition of the various metals and alloys, total number of days immersed in mine water, total loss, and loss per unit-area per day for each test specimen tested at the three mines. are given in tables 4, 5 and 6. Three specimens of each material were tested at each mine. Average figures, showing the loss in weight per unit area per day, for each class of material, are given in table 7.

TYPICAL CORRODED TEST SPECIMENS FROM EDNA NO. 2 MINE.

To show the appearance of the materials, after corrosion and subsequent cleaning in the laboratory, representative test specimens of each class of material were photographed and are shown in Plates II to XIII inclusive. All of the corroded test specimens shown are from the Edna No. 2 mine, and are typical of the material which they represent. The average acidity of the water from the Edna No. 2 mine during the test was 2160 parts per million of free sulphuric acid and 14,160 parts per million of free sulphuric acid plus sulphates of iron and aluminum.

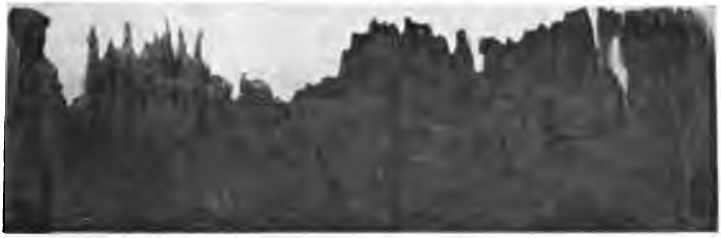
B-1. Cast leaded cupro-nickel.—Approximate composition; Cu, 50-60; Ni, 20-30; Pb, 20-30. Coating removable with difficulty; uniform corrosion. Days immersed, 135; loss in milligrams per sq. cm. per day, 4.14.

B-4. Cast chromium-iron cupro-nickel.—Approximate composition; Cu, 35-45; Ni, 35-45; Fe, 12-20; ferro-chromium 6-16. Coating removable with difficulty; uniform corrosion with some local pitting. Days immersed, 135; loss in milligrams per sq. cm. per day, 6.88.

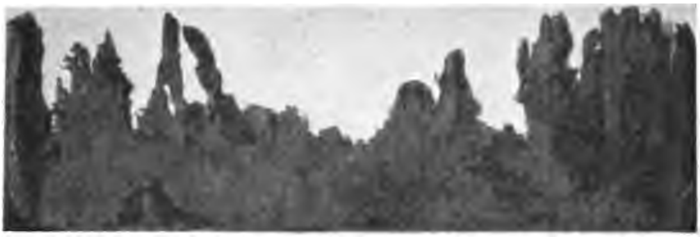
B-7. Cast tin-lead nickel silver.—Approximate composition; Cu, 60; Zn, 14; Ni, 15; Pb, 8; Sn, 3. Coating removable with difficulty; uniform corrosion. Days immersed, 135; loss in milligrams per sq. cm. per day, 4.27.

B-10. Cast silicon nickel silver.—Approximate composition; Cu, 49; Ni, 25; Zn, 25; Si, 1. Coating easily removable; considerable uniform corrosion. Days immersed, 135; loss in milligrams per sq. cm. per day, 7.13.

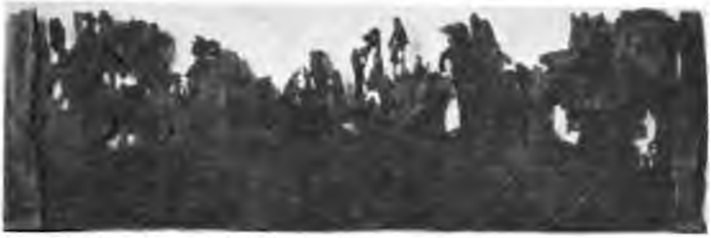
PLATE II.—*Typical test specimens after immersion in water from Edna No. 2 mine.*



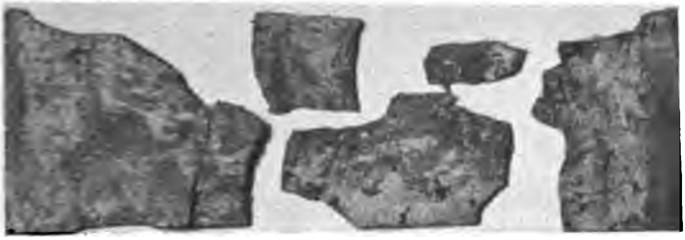
B-13. Rolled nickel silver.—Approximate composition; Cu, 63.8; Zn, 17.7; Ni, 18.5. Coating easily removable; considerable uniform corrosion. Days immersed, 65; loss in milligrams per cm. per day, 7.14.



B-16. Rolled high brass.—Approximate composition; Cu, 66.6; Zn, 33.4. Coating easily removable; considerable uniform corrosion. Days immersed, 65; loss in milligrams per sq. cm. per day, 7.38.

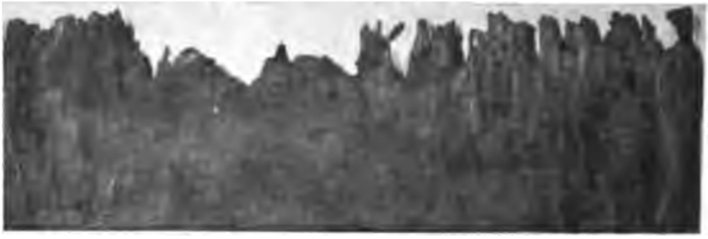


B-19. Rolled low brass.—Approximate composition; Cu, 80; Zn, 20. Coating easily removable; considerable uniform corrosion. Days immersed, 65; loss in milligrams per sq. cm. per day, 7.10.

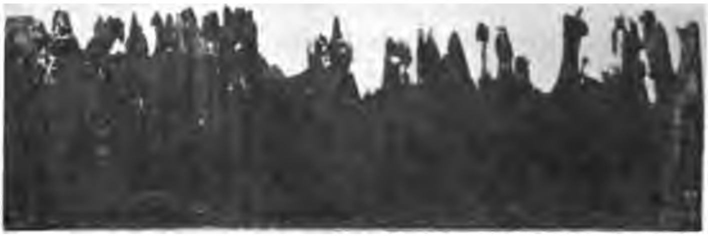


B-24. Rolled naval brass.—Approximate composition; Cu, 60.4; Zn, 38.8; Sn, 0.8. Coating removable with difficulty; pieces brittle and easily broken. Days immersed, 65; loss in milligrams per sq. cm. per day, 7.86.

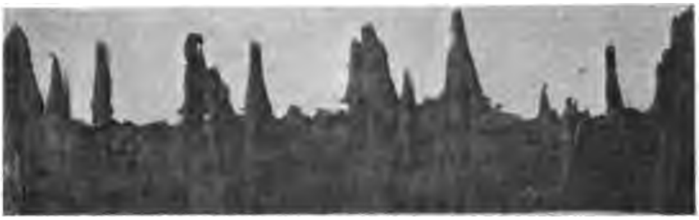
Plate III.—*Typical test specimens after immersion in water from Edna No. 2 mine—(Continued).*



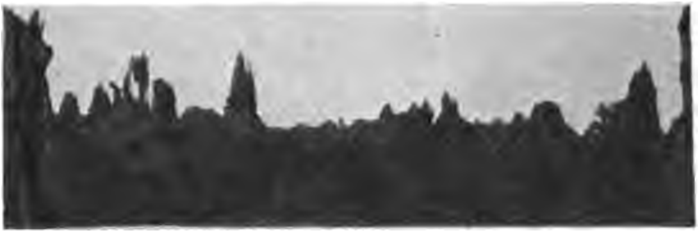
B-26 Rolled pure copper.—Coating easily removable; considerable uniform corrosion. Days immersed, 65; loss in milligrams per sq. cm. per day, 7.40.



B-28. Rolled brass. (Admiralty metal.)—Grain size 0.025 mm. Approximate composition; Cu, 70; Zn, 29; Sn, 1. Coating easily removable; considerable uniform corrosion. Days immersed, 65; loss in milligrams per sq. cm. per day, 7.08.

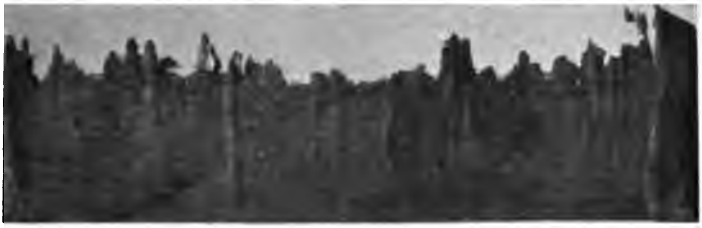


B-31. Rolled cupro-nickel.—Approximate composition; Cu, 85; Ni, 15. Coating easily removable; considerable uniform corrosion. Days immersed, 65; loss in milligrams per sq. cm. per day, 7.47.



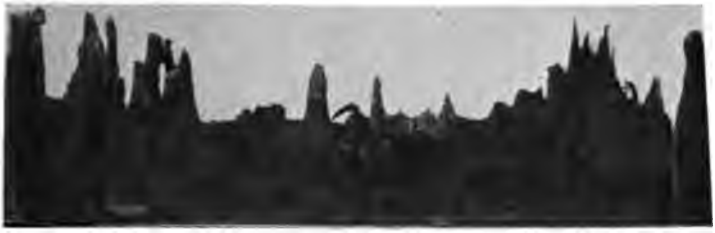
B-34. Rolled nickel silver.—Approximate composition; Cu, 52;Zn, 36; Ni, 12. Coating easily removable; considerable uniform corrosion. Days immersed, 65; loss in milligrams per sq. cm. per day, 7.29.

PLATE IV.—*Typical test specimens after immersion in water from Edna No. 2 mine—(Continued).*



B-37. Rolled cupro-nickel (coin metal.)—Approximate composition; Cu, 75; Ni, 25. Coating easily removable; considerable uniform corrosion. Days immersed, 65; loss in milligrams per sq. cm. per day, 7.39.

B-40. Rolled monel metal.—Approximate composition; Ni, 67; Cu, 28; Mn, 1.8; Fe, 1.8; C, 0.2, S, 0.03. Coating easily removable; considerable uniform corrosion. Days immersed, 79; loss in milligrams per sq. cm. per day, 6.79.

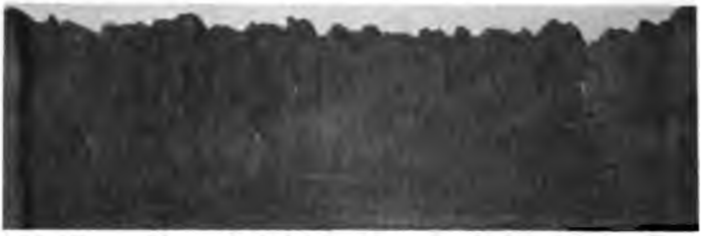


B-43. Rolled iron nickel silver.—Approximate composition; Cu, 60-70; Ni, 9-15; Zn, 20-25; Fe, 1-4. Coating easily removable; considerable uniform corrosion. Days immersed, 65; loss in milligrams per sq. cm. per day, 7.84.

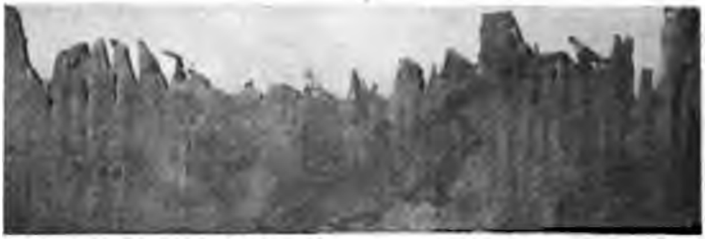
B-46. Rolled manganese bronze.—Approximate composition; Cu, 57-60; Zn, 37-40; Fe, 0.8-2.0; Sn, 0.5-1.5; Mn, 0.3 (maximum); Pb, 0.2 (maximum). Coating easily removable; considerable uniform corrosion; pieces brittle. Days immersed, 72; loss in milligrams per sq. cm. per day, 7.06.

PLATE V.—*Typical test specimens after immersion in water from Edna No. 2 mine—(Continued).*

B-49. Rolled zinc phosphor-bronze.—Approximate composition; Cu, 85-90; Sn, 6-11; Zn, 4 (maximum); P, 0.5 (maximum); Pb, 0.2 (maximum). Coating removable with difficulty; uniform corrosion. Days immersed, 135; loss in milligrams per sq. cm. per day, 2.06.



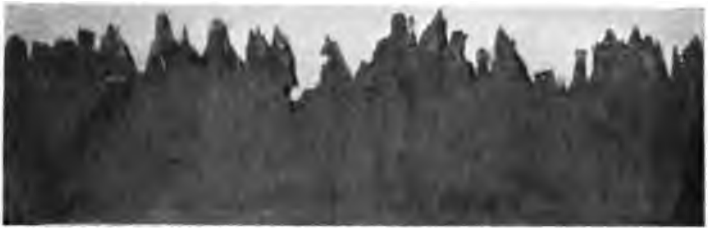
B-52. Rolled iron aluminum bronze.—Approximate composition; Cu, 85; Fe, 8; Al, 7. Coating easily removable; considerable uniform corrosion. Days immersed, 93; loss in milligrams per sq. cm. per day, 6.18.



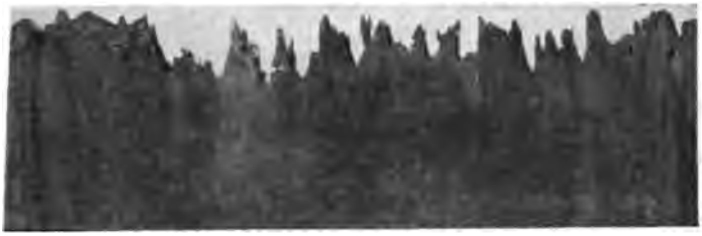
B-56. Rolled bronze.—Approximate composition; Cu, 98.7; Sn, 1.3. Coating easily removable; considerable irregular corrosion. Days immersed, 65; loss in milligrams per sq. cm. per day, 6.99.

B-58. Rolled phosphor-bronze.—Approximate composition; Cu, 94.4; Sn, 5.5; P, 0.1. Coating easily removable; considerable irregular corrosion. Days immersed, 79; loss in milligrams per sq. cm. per day, 4.99.

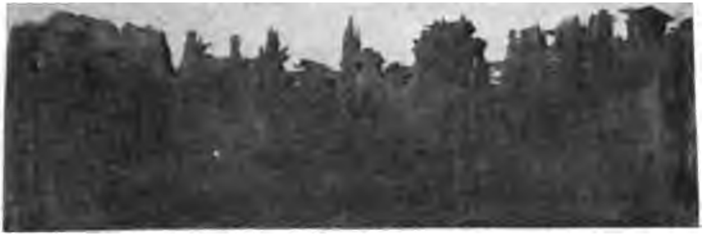
PLATE VI.—*Typical test specimens after immersion in water from Edna No. 2 mine—(Continued).*



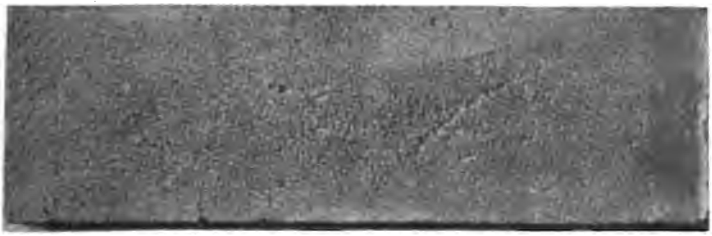
B-61. Rolled copper-manganese-iron alloy.—Approximate composition; Cu, 95; Mn, 4; Fe, 1. Coating easily removable; considerable uniform corrosion. Days immersed, 65; loss in milligrams per sq. cm. per day, 7.34.



B-65. Rolled brass (Admiralty metal).—Grain size, 0.035 mm. Approximate composition; Cu, 70; Zn, 29; Sn, 1. Coating easily removable; considerable corrosion; elongated, shallow pitting. Days immersed, 65; loss in milligrams per sq. cm. per day, 6.92.

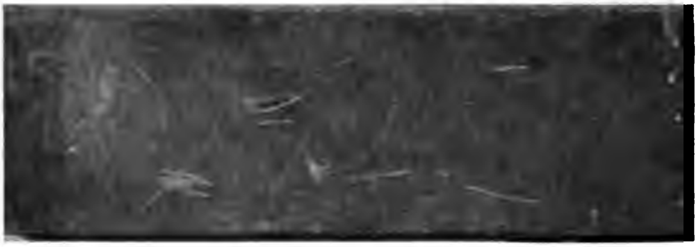


B-68. Rolled brass (Admiralty metal).—Grain size, 0.075 mm. Approximate composition; Cu, 78; Zn, 29; Sn, 1. Coating easily removable; considerable corrosion; elongated, shallow pitting. Days immersed, 65; loss in milligrams per sq. cm. per day, 6.78.

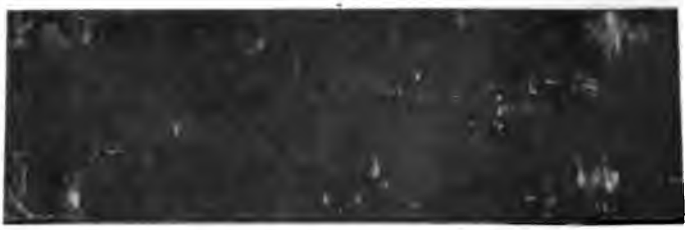


B-71. Cast copper-lead alloy.—Approximate composition; Cu, 50; Pb, 50. Coating easily removable; uniform corrosion with some irregular pittings. Days immersed, 121; loss in milligrams per sq. cm. per day, 3.94.

PLATE VII.—*Typical test specimens after immersion in water from Edna No. 2 mine—(Continued).*



B-73. Cast leaded zinc bronze.—Approximate composition; Cu, 86; Sn, 12; Zn, 1.5; Pb, 0.5. Coating not removable; uniform corrosion. Days immersed, 135; loss in milligrams per sq. cm. per day, 0.76.



B-76. Cast aluminum bronze.—Approximate composition; Cu, 90; Al, 10. Coating removable with difficulty; irregular corrosion. Days immersed, 135; loss in milligrams per sq. cm. per day, 5.14.

B-79. Cast bronze.—Approximate composition; Cu, 90; Sn, 10. Coating partly removable; irregular corrosion. Days immersed, 135; loss in milligrams per sq. cm. per day, 1.90.

B-82. Cast leaded bronze.—Approximate composition; Cu, 88.1; Sn, 9.9; Pb. 2.0. Coating removable with difficulty; irregular corrosion. Days immersed, 135; loss in milligrams per sq. cm. per day, 3.01.

PLATE VIII.—*Typical specimens after immersion in water from Edna No. 2 mine—(Continued).*

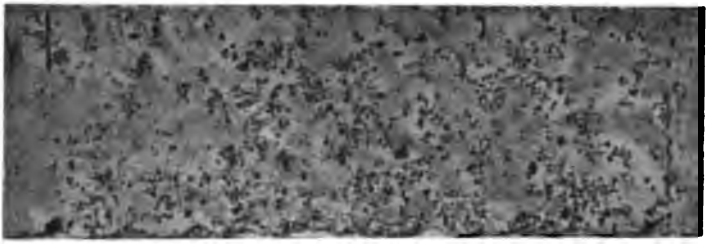
B-86. Cast leaded bronze.—Approximate composition; Cu, 75; Sn, 10; Pb, 15. Coating partly removable; irregular corrosion. Days immersed, 135; loss in milligrams per sq. cm. per day, 1.28.

B-88. Cast aluminum-silicon alloy.—Approximate composition; Al, 95; Si, 5. Coating removable with difficulty; considerable irregular pitting. Days immersed. 72; loss in milligrams per sq. cm. per day, 2.19.

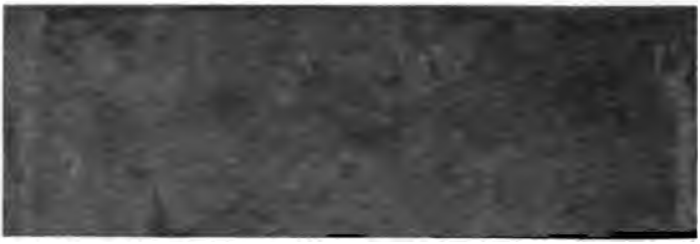
B-91. Cast aluminum-manganese alloy.—Approximate composition; Al, 98; Mn, 2. No coating; irregular pitting. Days immersion, 72; loss in milligrams per sq. cm. per day, 2.23.

B-94. Rolled aluminum-manganese alloy.—Composition not furnished. No coating; irregular pitting. Days immersion, 7; loss in milligrams per sq. cm. per day, 2.64.

PLATE IX.—*Typical test specimens after immersion in water from Edna No. 2 mine—(Continued).*



B-97. Rolled aluminum alloy.—Composition not furnished. No coating; irregular corrosion with pitting. Days immersion, 51; loss in milligrams per sq. cm. per day, 1.82.

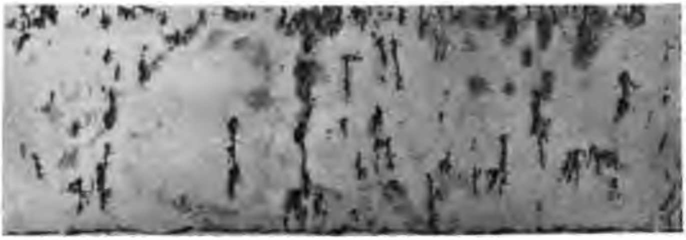


B-100. Rolled rustless steel "A."—Approximate composition; highly alloyed chromium-nickel-silicon steel. No coating; no visible corrosion. Days immersed, 135; loss in milligrams per sq. cm. per day, 0.00045.

B-103. Rolled rustless steel "B".—Approximate composition; highly alloyed chromium-nickel-silicon steel. No coating; no visible corrosion. Days immersed, 135; loss in milligrams per sq. cm. per day, 0.00089.

B-106. Rolled high chromium rustless steel.—Approximate composition; Cr, 29.5; Si, 0.53; Mn, 0.27; C, 0.36. No coating; no visible corrosion. Days immersed, 135; loss in milligrams per sq. cm. per day, 0.00045.

PLATE X.—*Typical test specimens after immersion in water from Edna No. 2 mine—(Continued).*



B-109. Rolled pure aluminum.—Coating easily removable; irregular pitting. Days immersed, 21; loss in milligrams per sq. cm. per day, 1.55.

B-113. Cast iron-manganese cupro-nickel.—Approximate composition; Cu, 75; Ni, 15; remainder, Fe and Mn (proportions not furnished). Coating easily removable; considerable uniform corrosion. Days immersed, 135; loss in milligrams per sq. cm. per day, 7.27.

B-115. Rolled pure ingot iron.—Approximate composition; Fe, 99.9. Coating removable with difficulty; considerable uniform corrosion. Days immersed, 35; loss in milligrams per sq. cm. per day, 6.89.

B-119. Rolled nichrome.—Approximate composition; Ni, 58-62; Cr, 12-14; Fe, 25; Mn, 1.25-1.50; Si, 0.5. No coating; no visible corrosion. Days immersed, 135; loss in milligrams per sq. cm. per day, 0.00184.

PLATE XI.—*Typical test specimens after immersion in water from Edna No. 2 mine—(Continued).*

B-122. Rolled nickel.—Approximate composition; Ni, 99. Coating not removable. Days immersed, 135; loss in milligrams per sq. cm. per day, 0.0028.

B-130. High silicon cast iron.—Approximate composition; Si, 13-14; graphitic carbon, 1.3; remainder, Fe. Coating partly removable; uniform corrosion. Days immersed, 135; loss in milligrams per sq. cm. per day, 0.60.

B-133. High-silicon cast iron.—Approximate composition; Si, 14-14.5; C, 0.2-0.6; Mn, 0.35; P, 0.16-0.20; S, 0.05 (maximum). Coating not removable; no visible corrosion. Days immersed, 135; loss in milligrams per sq. cm. per day, 0.0054.

B-136. Cast tin-lead nickel silver.—Approximate composition; Cu, 57; Ni, 19.5; Zn, 16; Pb, 6; Sn, 2. Coating removable with difficulty; uniform corrosion. Days immersed, 56; loss in milligrams per sq. cm. per day, 4.84.

PLATE XII.—*Typical test specimens after immersion in water from Edna No. 2 mine—(Continued).*

B-139. Rolled nickel-chromium-iron alloy.—Approximate composition; Ni, 65; Cr, 16; Mn, 0.7; Si, 0.7; Al, 0.15; remainder, Fe. Coating easily removable; irregular corrosion with pitting. Days immersed, 42; loss in milligrams per sq. cm. per day, 7.20. (This material was furnished in pieces only 1 inch in width.)

PLATE XIII.—*Typical test specimen after immersion in water from Edna No. 2 mine—(Continued).*

DISCUSSION OF CORROSION TESTS.

It must be remembered that no satisfactory method of making comparative corrosion tests has been standardized. Some materials develop serious local pitting, and may still show a small loss in weight, while other materials corrode uniformly with no pronounced pitting, and in these cases the loss in weight may be relatively large. By considering both the loss in weight per unit-area and the nature of corrosion—whether uniform or irregular—a fair comparison may be made as to the relative worth of the different materials for resisting the corrosive action of acid mine water. A tabulated description of the appearance of the test specimens after the test is given in table 8. This table shows the nature of the corrosion, and should be used in conjunction with tables 4, 5, 6, and 7, which give the loss in weight.

The method of cleaning the test pieces after the test must also be considered. In most instances the coatings caused by corrosion were removed by rubbing with a fiber brush; however, in some instances they were quite hard and adhered strongly to the metal, and in such instances the coatings were not entirely removed before weighing. Such coatings are designated in table 8 as not removable. In studying the results of the tests, table 8, describing the appearance of the corroded specimens, should be used in conjunction with those giving the loss in weight and reference should also be made to the photographs.

All alloys of the brass type tested, containing considerable amounts of zinc, were corroded extensively by the mine waters. These materials were uniformly corroded, and showed a large loss in weight.

Bronzes containing considerable tin were also corroded, but to a less extent than the brasses. Evidently copper-zinc alloys of the brass type are less desirable for use in mine water than copper-tin alloys. The bronzes which contained relatively small amounts of tin were, as a rule, corroded more than those high in tin. At the present time, bronzes are largely used for parts in pumps designed for handling acid water from coal mines.

Copper-nickel alloys of the cupro-nickel type were corroded to about the same extent as the brasses. These alloys showed a large loss in weight and were uniformly corroded.

The nickel-silver alloys, which contained copper, zinc, and nickel, were also badly corroded—the corrosion in most instances being uniform.

The aluminum alloys tested showed a marked tendency to pronounced pitting. These alloys show a comparatively small loss in weight, but are not suitable for use in mine water owing to rapid pitting.

The materials which showed practically no corrosion in the mine waters include a high chromium steel (test specimens 106, 107, and 108), two highly alloyed chromium-nickel-silicon steels (test specimens 100, 101, 102, 103, 104, and 105), a high-silicon cast iron (test specimens 133, 134, and 135), and a nickel-chromium-iron alloy (test specimens 118, 119, and 120). It is interesting to note that all of these materails, except the high-silicon cast iron, contain large amounts of chromium. These resistant materials have certain disadvantages for general use in coal-mine equipment, such as the brittleness and hardness of the high-silicon cast iron and the relatively high cost of the others; however, these resistant materials should prove satisfactory for use in such pump parts and other equipment where these factors are not a serious consideration.

Pure nickel showed very little corrosion in the water from the Edna No. 2 mine—the water highest in acidity—but showed considerable corrosion in the waters from the Montour No. 1 and Calumet mines.

While the essential qualification of metals and alloys for use in coal-mine equipment, such as pumps and their parts, is resistance to corrosion by the acid water, other important considerations are cost and physical characteristics of the material. Drysdale[15] states that a true acid-resisting alloy to be an industrial success should also be a good foundry metal—for instance, one that gives a dense structure, free from a tendency toward segregation on cooling; pours well; does not oxidize excessively in melting; does not burn the sand in pouring; takes a good impression of the mold; has a normal shrinkage; and gives castings which are easily cleaned. The metal or alloy should also be good for machine-shop working, and should have certain physical properties which are under control, enabling the manufacturer to comply with any reasonable specifications that may be called for, such as degrees of toughness, malleability and strength. It must also be reasonable in cost. Rowe[16] gives similar qualifications, and also states that there are no corrosion-resisting alloys which do not fail in some or all of these particulars.

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[15] Drysdale, G. A., Seeks better acid-resisting alloys: Foundry, vol. 49, No. 24, 1922, p. 976.

Questionnaires were sent to the different manufacturers who supplied test specimens for the mine-water corrosion tests, in order to obtain data as to the physical properties of the materials submitted, and the information given in their replies is shown in table 9.

PHENOMENA OBSERVED DURING TESTS.

Formation of coatings.—A large number of test specimens were covered with a coating during a major portion of the test. It is difficult to differentiate between a precipitate from the mine water and a coating formed by a change in the surface of the metal. The term "coating" is used here in a broad sense to denote all reaction products formed on the surface of the specimen.

One of the bronzes—test specimen numbers 73, 74, and 75—is a typical example of an alloy on which a closely adhering coating was formed. The surfaces remained hard. The parallel grooves formed in machining the test pieces remained visible throughout the test. A change in color was observed, but it was not until the pieces were removed from the mines and cleaned that it became definitely evident that a coating had been formed. Other materials exhibited similar characteristics.

Some materials had rather thick, soft, fine-grained coatings. The test specimens during the test appeared as when first immersed except for a change in color and luster. These coatings adhered fairly tight, but could be readily removed with a fiber brush and water.

A large number of the test specimens had loosely adhering coatings, and these could be readily removed by rinsing in water and rubbing with the hand.

It seems evident that in some cases the coating acts as a protection against further corrosion, or at least retards the action. This effect was demonstrated in several cases. On several test specimens having hard closely adhering coatings, small portions of the coatings were removed during the course of the test. After the specimens had been removed and cleaned, it was noted that corrosion had proceeded to a greater depth over the area which had been cleaned at the mine during the course of the test. For example, see test specimen B 86, Plate IX.

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[16] Rowe, F. W., The resistance of industrial alloys to corrosion by liquids: Metal Ind., London, vol. 20, No. 11, 1922, p. 263.

Effect of the rate of water flow.—At the Montour No. 1 mine the wooden racks containing the test specimens were placed on edge when immersed in the mine sump. It was observed that the edges toward the flow of water corroded much faster than the other edges. At the Calumet and Edna No. 2 mines the racks were placed in wooden boxes as shown in figure 1. It was noted that the edges of the test specimens nearest the surface corroded the most. This was probably due to the fact that the upper edges of the specimens were subjected to a slightly greater velocity of water flow than the lower part of the specimens. The upper edges of the test specimens shown in Plates II to XIII are the upper edges as arranged in the test-boxes during the corrosion test.

It seems from the accumulated data, that when the rate of water flow is maintained constant, the rate of corrosion, in the majority of cases, is a function of the acidity of the water. The rate of water flow at the Edna No. 2 and Calumet mines was maintained constant throughout the tests, and it is found that the ratios of the average total and free acidities to the average loss of all the materials tested per unit-area per day are the same for each mine. This does not hold true for the Montour No. 1 mine, where the rate of water flow was not the same as at the other mines.

In acid mine water, the rate of corrosion mainly depends upon the variable factors,—namely, rate of water flow, and acidity of the water. The total loss in weight per unit-area will also depend upon the effect of the erosive material carried by the water.

Selective corrosion.—In some alloys, one constituent goes into solution at a faster rate than the other metals—that is, it has a higher solution pressure. This is particularly true of alloys high in zinc, this metal tending to go into solution very rapidly in dilute sulphuric acid.

At the Montour No. 1 mine it was observed that the low brass test specimens (A 19, A 20, and A 21), were covered with nodules of copper crystals. These specimens were examined under a miscroscope, using a low magnification. In seems probable that these crystals were deposited from solution, rather than being copper *in situ* from the original brass. As corrosion proceeded, the copper was evidently deposited from solution, the zinc remaining in solution. The rate of flow was sufficiently slow to permit the growth of copper crystals and the formation of aggregates, or nodules, of the crystals. Test specimen A 19 was removed for study during the test. Test specimens A 20 and A 21 were removed later, as they failed. Upon examination of specimens A 20 and A 21 it was found that the nodules had been acted upon by the acid mine water. On specimen A 19 the nodules had not been visibly attacked at the time of its removal.

Effect of grain size.—Three groups of Admiralty tube metal, differing in grain size, but of the same chemical composition, were included in the test. The results of the tests on these metals are noted in the tables. In this case the difference in grain size had no noticeable effect upon the rate of corrosion. However, it is not advisable to draw any definite conclusion from so little data, and this subject needs further investigation.

Formation of pits.—Test specimens that were pitted previous to immersion were sketched and the position of pits noted. These pits did not seem to accelerate corrosion, as might have been expected.

Test pieces after cleaning were examined under a microscope with low magnification. In some cases pits of small size were noted, but these are not recorded in table 8.

The aluminum-silicon alloy (test specimens 88 to 90), and the aluminum-manganese alloy (test specimens 91 to 93), formed large pits and had a honeycomb appearance.

Segregated groups of pits, with pinholes through the metal, were noted in the pure aluminum test specimens 109, 110, and 111; and in the aluminum alloy test specimens 94 to 99 inclusive. On some pieces a raised patch or nodule of metal was left above the corroded surface of the test piece. This phenomena is noted in table 8 under the head of "Irregular corrosion." A pit sometimes occurred in the patch, giving the effect of a crater within a cone.

Admiralty metal test specimens 64 to 69 inclusive afford an example of another type of pitting, the pits being elongated, shallow, and parallel to the length of the piece.

Effect of strain.—The numbers stamped on each test specimen effected a strain in the surrounding material. In the case of ingot iron the numbers were the first portions of the test specimens to be eaten through. The effect of strain did not appar to make any appreciable difference in the corrosion of the other materials tested.

Comparative nature of corrosion at the different mines.—Test specimens of the same chemical composition exhibited the same characteristics in the various mines, differing only in the degree of corrosion. Exceptions to this were low brass which showed nodules of copper at the Montour No. 1 mine, and did not at the Calumet and Edna No. 2 mines. At the Calumet mine the rustless steels (test specimens 100 to 105) were stained and slightly corroded;

whereas at the Edna No. 2 and Montour No. 1 mines the corrosion loss was very small, and no stains appeared.

SUMMARY AND CONCLUSIONS.

Forty-five different metals and alloys were subjected to corrosion tests in mine water at three coal mines in the western Pennsylvania coal region—namely, the Montour No. 1 mine of the Pittsburgh Coal Co., at Southview, Washington County, Pa.; the Edna No. 2 mine of the Hillman Coal & Coke Co., at Wendel, Westmoreland County, Pa.; and the Calumet mine of the H. C. Frick Coke Co., at Calumet, Westmoreland County, Pa.

At the Montour No. 1 mine the test covered a period of 119 days, the average acidity of the water being 1430 parts per million free sulphuric acid and 11,360 parts per million free sulphuric acid plus sulphates of iron and aluminum. The test covered a period of 135 days at the Edna No. 2 mine, the average acidity of the water being 2160 parts per million free sulphuric acid and 14,160 parts per million free sulphuric acid plus sulphate of iron and aluminum. At the Calumet mine the test covered a period of 98 days, the average acidity of the water being 430 parts per million free sulphuric acid and 2,950 parts per million free sulphuric acid plus sulphates of iron and aluminum.

Three test specimens of each type of material were completely immersed in flowing mine water at each of the mines. At the Montour No. 1 mine the test specimens were placed in the mine sump in slowly flowing water. At the Calumet and Edna mines the test specimens were placed in wooden boxes, and the water flow surrounding the test specimens was regulated to a velocity of 1.8 inches per minute.

All alloys tested of the brass type, containing considerable zinc, were corroded extensively by the mine waters. Bronzes, containing considerable tin, were also corroded, but to a less extent than the brasses. Evidently copper-zinc alloys are less desirable for use in mine water than copper-tin alloys.

Cupro-nickel alloys were corroded about to the same amount as the brasses. Nickel silver alloys, which contain copper, zinc, and nickel, were also corroded extensively. Aluminum alloys showed a marked tendency to pronounced pitting.

The materials which showed a marked resistance to the corrosive action of the acid mine waters include a high chromium steel. two highly alloyed chromium-nickel-silicon steels, a high-silicon cast iron, and a nickel-chromium-iron alloy. All of these materials, except the high-silicon cast iron, contain large amounts of chromium. These resistant materials have certain disadvantages for general use in coal-mine equipment, such as the brittleness and hardness of the high-silicon cast iron and the relatively high cost of the others; however, these resistant materials should prove satisfactory for use in such pump parts and other equipment where these factors are not a serious consideration.

Economic considerations, such as cost, ease of fabrication, and physical properties, will be factors in determining the suitability of a metal or alloy for use in equipment exposed to the action of acid mine water.

Following are tables 4 to 9, inclusive, referred to on pages 21, 33, and 35, covering the composition and loss in weight of test pieces at the three mines, general appearance of the test pieces, and the physical properties of the metals and alloys used:

TABLE 4.—*Composition and loss in weight of test specimens exposed to action of Montour No. 1 mine water.*

Test piece number.	Designation.	Approximate chemical composition[a], per cent.	Date.		Days immersed.	Weight, in grams.		Loss in weight, in grams.	Dimensions of test specimens, in inches.	Area of test specimens, in square inches.	Loss in milligrams, per sq. inch per day.	Loss in milligrams, per sq. cm. per day.
			Immersed.	Removed.		Before immersion.	After immersion.					
1	2	3	4	5	6	7	8	9	10	11	12	13
	BRASSES.											
A 16	Rolled high brass..		Dec. 5, 1921	April 3, 1922	119	85.77	49.85	35.92	0.05 x2.00x6.01	24.84	12.151	1.88
A 17	" " " ..	Cu 66.6.............	"	"	"	85.43	49.77	35.66	0.05 x2.00x6.01	24.84	12.058	1.87
A 18	" " " ..	Zn 33.4.............	"	"	"	84.81	49.11	35.70	0.05 x2.00x6.01	24.84	12.075	1.87
Average	" " " ..				"	85.34	49.58	35.76	....	24.84	12.095	1.87
A 19[b]	Rolled low brass..		"	Jan. 31, 1922	57	86.18	62.08	24.10	0.05 x2.00x6.05	25.01	16.905	2.62
A 20	" " " ..	Cu 80...............	"	Mar. 6, 1922	90	86.27	54.89	31.38	0.05 x2.00x6.04	24.96	13.968	2.17
A 21	" " " ..	Zn 20...............	"	"	90	84.84	53.66	31.18	0.05 x2.00x6.04	24.96	13.878	2.15
Average	" " " ..				79	85.76	56.88	28.89	....	24.98	14.917	2.31
A 22	Rolled Naval brass	Cu 60.0.............	"	April 3, 1922	119	86.34	60.95	25.39	0.051x2.00x6.00	24.82	8.595	1.33
A 23	" " "	Zn 38.8.............	"	"	"	80.92	56.93	23.99	0.049x2.00x6.00	24.78	8.121	1.26
A 24	" " "	Sn 0.8.............	"	"	"	81.71	57.60	24.11	0.049x2.00x6.00	24.78	8.162	1.27
Average	" " "				"	82.99	58.49	24.50	....	24.79	8.293	1.29
A 28	Rolled brass		"	"	"	84.97	51.26	33.71	0.05 x2.01x6.02	25.00	11.327	1.76
A 29	(Admiralty metal),	Cu 70, Sn 1...........	"	"	"	85.66	54.64	31.02	0.051x2.01x6.03	25.06	10.394	1.61
A 30	grain size	Zn 29	"	"	"	86.19	53.17	33.02	0.051x2.01x6.02	25.02	11.084	1.72
Average	0.025 mm.........				"	85.61	53.02	32.58	....	25.03	10.935	1.70
A 64	Rolled brass		"	"	"	86.54	53.62	32.92	0.05 x2.01x6.01	24.96	11.075	1.72
A 65	(Admiralty metal),	Cu 70, Zn 29..........	"	"	"	86.42	55.26	31.16	0.05 x2.01x6.02	25.00	10.470	1.62
A 66	grain size	Sn 1	"	"	"	86.46	56.06	30.40	0.05 x2.01x6.02	25.00	10.218	1.58
Average	0.035 mm........				"	86.47	54.98	31.49	....	24.99	10.587	1.64
A 67	Rolled brass		"	"	"	88.77	54.55	34.22	0.053x2.01x6.02	25.05	11.478	1.78
A 68	(Admiralty metal),	Cu 70, Zn 29..........	"	"	"	88.81	57.32	31.49	0.052x2.01x6.02	25.04	10.563	1.64
A 69	grain size	Sn 1	"	"	"	90.73	58.82	31.91	0.053x2.01x6.02	25.05	10.705	1.66
Average	0.075 mm.........				"	89.44	56.90	32.54	....	25.05	10.915	1.70

A 46	Rolled manganese	Cu 57-60, Zn 37-40....	"	"	"	112.80	82.96	29.84	0.067x2.02x6.03	25.44	9.848	1.53
A 47	bronze..........	Sn 0.5-1.5, Fe 0.8-2,	"	"	"	113.22	84.44	28.78	0.067x2.02x6.03	25.44	9.504	1.47
A 48	Rolled manganese	Mn 0.3 (maximum)....	"	"	"	114.44	85.90	28.54	0.07 x2.02x6.04	25.53	9.386	1.45
Average	bronze..........	Pb 0.2 (maximum)....			"	113.49	84.43	29.05	....	25.47	9.579	1.48
	BRONZES.											
A 79	Cast bronze......		"	"	"	280.64	269.27	11.37	0.17 x1.96x5.96	26.05	3.667	0.57
A 80	" "	Cu 90...............	"	"	"	281.61	266.33	15.28	0.17 x1.96x5.97	26.10	4.919	0.76
A 81	" "	Sn 10...............	"	"	"	281.38	268.69	12.69	0.17 x1.96x5.97	26.10	4.085	0.63
Average	" "				"	281.21	268.10	13.11	....	26.08	4.224	0.66
A 55	Rolled bronze.....		"	"	"	84.98	48.42	36.56	0.05 x2.01x6.01	24.96	12.302	1.91
A 56	" "	Cu 98.7.............	"	"	"	85.79	54.10	31.69	0.05 x2.01x6.01	24.96	10.663	1.65
A 57	" "	Sn 1.3.............	"	"	"	86.08	54.14	31.94	0.05 x2.01x6.01	24.96	10.747	1.67
Average	" "				"	85.62	52.22	33.40	....	24.96	11.237	1.74
A 58	Rolled phosphor	Cu 94.4.............	"	"	"	91.42	71.71	19.71	0.05 x2.01x6.02	25.00	6.625	1.03
A 59	bronze...........	Sn 5.5.............	"	"	"	90.84	74.71	16.13	0.05 x2.01x6.02	25.00	5.421	0.84
A 60	Rolled phosphor	P 0.1.............	"	"	"	90.74	78.93	11.81	0.05 x2.01x6.02	25.00	3.969	0.62
Average	bronze...........				"	91.00	75.12	15.88	....	25.00	5.338	0.83
A 49	Rolled phosphor-	Cu 85-90, Zn 4 max.	"	"	"	112.04	90.16	21.88	0.06 x2.01x6.02	25.16	7.307	1.13
A 50	zinc bronze.......	Sn 6-11, Pb 0.2 max.	"	"	"	112.35	98.38	13.97	0.06 x2.01x6.03	25.20	4.658	0.72
A 51	Rolled phosphor-	P 0.5 max..........	"	"	"	111.23	95.60	15.63	0.06 x2.01x6.01	25.12	5.288	0.82
Average	zinc bronze.......				"	111.87	94.71	17.16	....	25.16	5.751	0.89
A 73	Cast leaded zinc		"	"	"	342.14	338.74	3.40	0.21 x1.96x5.98	26.77	1.161	0.18
A 74	bronze...........	Cu 86, Pb 0.5........	"	"	"	337.81	335.18	2.63	0.21 x1.96x5.98	26.77	.825	0.13
A 75	Cast leaded zinc	Sn 12, Zn 1.5........	"	"	"	344.75	341.61	3.14	0.21 x1.96x5.98	26.77	.984	0.15
Average	bronze...........				"	341.57	338.51	3.06	....	26.77	.990	0.15
A 85	Cast leaded bronze	Cu 75...............	"	"	"	412.52	396.94	15.58	0.24 x1.97x6.00	27.47	4.765	0.74
A 86	" " "	Sn 10...............	"	"	"	413.19	400.16	13.03	0.25 x1.97x6.00	27.68	3.962	0.61
A 87	" " "	Pb 15...............	"	"	"	413.52	400.38	13.14	0.25 x1.97x6.00	27.63	3.995	0.62
Average	" " "				"	418.08	399.16	13.92	....	27.58	4.241	0.66
A 82	Cast leaded bronze	Cu 88.1.............	"	"	"	373.68	357.75	15.93	0.22 x1.98x5.95	27.05	4.948	0.77
A 83	" " "	Sn 9.9.............	"	"	"	382.53	372.37	10.16	0.23 x1.98x5.95	27.21	3.137	0.49
A 84	" " "	Pb 2.0.............	"	"	"	373.71	362.65	11.06	0.22 x1.98x5.95	27.05	3.435	0.53
Average	" " "				"	376.64	364.26	12.38	....	27.10	3.840	0.60
	CUPRO-NICKEL.											
A 37	Rolled cupro-nickel		"	"	"	88.90	58.08	30.82	0.05 x2.01x5.99	24.88	10.403	1.61
A 38	(coin metal).......	Cu 75...............	"	"	"	89.41	60.24	29.17	0.05 x2.01x6.01	24.96	9.815	1.52
A 39	Rolled cupro-nicke	Ni 25...............	"	"	"	88.97	59.13	29.84	0.05 x2.01x6.00	24.92	10.058	1.56
Average	(coin metal)......				"	89.09	59.15	29.94	....	24.92	10.092	1.56

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[a] *The chemical compositions, as given, were submitted by the manufacturers and are in most instances only approximate type compositions.*

[b] *This test specimen was removed for study.*

TABLE 4.—*Composition and loss in weight of test specimens exposed to action of Montour No. 1 mine water—Continued.*

Test piece number.	Designation.	Approximate chemical composition[a], per cent.	Date.		Days immersed.	Weight, in grams.		Loss in weight, in grams.	Dimensions of test specimens, in inches.	Area of test specimens, in square inches.	Loss in milligrams, per sq. inch per day.	Loss in milligrams, per sq. cm. per day.
			Immersed.	Removed.		Before immersion.	After immersion.					
1	2	3	4	5	6	7	8	9	10	11	12	13
	CUPRO-NICKEL.											
A 31	Rolled cupro-nicke	Cu 85 Ni 15	Dec. 5, 1921	April 3, 1922	119	84.45	51.92	32.53	0.047x2.01x6.00	24.87	10.991	1.70
A 32	" " "		"	"	"	85.02	53.36	31.66	0.047x2.01x6.02	24.95	10.655	1.65
A 33	" " "		"	"	"	87.13	55.56	31.57	0.048x2.01x6.03	25.01	10.605	1.65
Average	" " "				"	85.53	53.61	31.92	....	24.94	10.750	1.67
A 1	Cast leaded cupro-nickel	Cu 50-60 Ni 20-30 Pb 20-30	"	"	"	589.44	563.04	26.40	0.34 x1.96x5.97	28.79	7.705	1.19
A 2			"	"	"	504.65	482.57	22.08	0.34 x1.96x6.00	28.93	6.413	0.99
A 3	Cast leaded cupro-nickel		"	"	"	602.48	573.90	28.58	0.34 x1.96x6.00	28.93	8.300	1.29
Average					"	565.52	539.84	25.69	....	28.88	7.463	1.16
A 4	Cast chromium iron cupro-nickel	Cu 35-45, Ni 35-45 Fe 12-20 Ferro-Chromium 6-16	"	"	"	515.86	484.35	31.51	0.34 x1.90x5.97	28.04	9.436	1.43
A 5			"	"	"	517.62	486.26	31.36	0.34 x1.91x5.97	28.17	9.352	1.45
A 6	Cast chromium iron cupro-nickel		"	"	"	516.63	485.52	31.11	0.34 x1.91x5.97	28.17	9.277	1.44
Average					"	516.70	485.38	31.33	....	28.13	9.355	1.44
A112	Cast iron manganese cupro-nickel	Cu 75 Ni 15 Fe and Mn, Balance	"	"	"	209.33	165.90	43.43	0.12 x1.99x6.00	25.80	14.142	2.19
A113			"	"	"	206.70	163.85	42.85	0.12 x1.99x6.00	25.80	13.949	2.16
A114			"	"	"	212.95	180.34	32.61	0.125x1.99x6.01	25.92	10.571	1.64
Average					"	209.66	170.03	39.63	....	25.84	12.887	2.00
	NICKEL SILVER.		"	"								
A 13	Rolled nickel silver	Cu 63.8 Zn 17.7 Ni 18.5	"	"	"	87.03	55.82	31.21	0.051x2.01x6.04	25.10	10.445	1.62
A 14	" " "		"	"	"	87.37	55.99	31.38	0.05 x2.01x6.04	25.09	10.504	1.63
A 15	" " "				"	87.37	55.93	31.44	0.05 x2.01x6.04	25.09	10.527	1.63
Average	" " "				"	87.26	55.91	31.34	....	25.09	10.492	1.63
A 43	Rolled iron nickel silver	Cn 60-70, Ni 9-15 Zn 20-25, Fe 1- 4	"	"	"	91.58	58.98	32.60	0.054x1.98x6.03	24.62	11.126	1.72
A 44			"	"	"	91.45	59.18	32.27	0.054x2.02x6.03	25.28	10.747	1.67
A 45	Rolled iron nickel silver		"	"	"	90.66	58.49	32.17	0.053x2.00x6.03	24.97	10.823	1.68
Average					"	91.23	58.88	32.35	....	24.94	10.899	1.69

A 84	Rolled nickel silver	Cu 52	"	"	"	83.54	50.32	33.22	0.05 x2.00x6.00	24.80	11.252	1.74
A 85	" " "	Zn 36	"	"	"	82.83	50.15	32.68	0.05 x2.00x6.00	24.80	11.067	1.72
A 86	" " "	Ni 12	"	"	"	83.48	50.61	32.87	0.05 x2.00x6.00	24.80	11.134	1.73
Average	" " "				"	83.28	50.36	32.92	....	24.80	11.151	1.73
A 10	Cast silicon nickel		"	"	"	199.89	162.96	36.93	0.12 x1.98x6.00	25.68	12.084	1.87
A 11	silver	Cu 49, Zn 25	"	"	"	212.43	180.98	31.45	0.13 x1.97x6.00	25.71	10.278	1.59
A 12	Cast silicon nickel	Ni 25, Si 1	"	"	"	199.20	165.59	33.61	0.12 x1.95x6.00	25.31	11.158	1.73
Average	silver				"	203.84	169.84	33.99	....	25.57	11.168	1.73
A 7	Cast tin-lead nickel	Cu 60, Zn 14	"	"	"	327.84	305.02	22.82	0.195x1.95x5.99	26.43	7.255	1.13
A 8	silver	Ni 15, Pb 8	"	"	"	327.72	306.14	21.58	0.195x1.95x5.99	26.43	6.860	1.06
A 9	Cast tin-lead nickel	Sn 3	"	"	"	326.85	305.56	21.29	0.195x1.95x5.99	26.43	6.768	1.05
Average	silver				"	327.47	305.57	21.90	....	26.43	6.961	1.08
A136	Cast tin-lead nickel	Cu 57, Ni 19.5	Mar. 6, 1922	"	28	440.98	436.77	4.21	0.26 x2.00x5.98	28.07	5.356	0.83
A137	silver	Sn 2, Zn 16	"	"	"	438.72	434.40	4.32	0.26 x2.00x5.98	28.07	5.496	0.85
A138	Cast tin-lead nickel	Pb 6	"	"	"	448.13	443.48	4.65	0.26 x2.00x5.99	28.11	5.907	0.92
Average	silver				"	442.61	438.22	4.39	....	28.08	5.586	0.87
	ALUMINUM ALLOYS.											
A 88	Cast Al-Si alloy		Dec. 5, 1921	Mar. 6, 1922	90	117.65	78.00	39.65	0.23 x1.99x5.99	27.51	16.011	2.48
A 89[b]	" " "	Al 95	"	"	"	117.72	80.30	37.42	0.23 x1.98x5.99	27.39	15.177	2.35
A 90[b]	" " "	Si 5	"	"	"	......	......	.....	0.23 x1.98x5.99	....	......	......
Average	" " "				"	117.69	79.15	38.54	....	27.45	15.594	2.42
A 91	Cast Al-Mn alloy		"	April 3, 1922	119	116.24	98.73	17.51	0.23 x1.98x5.92	27.07	5.435	0.84
A 92	" " "	Al 98	"	"	"	116.89	99.47	17.42	0.23 x1.98x5.92	27.07	5.407	0.84
A 93	" " "	Mn 2	"	"	"	116.53	99.38	17.15	0.23 x1.98x5.91	27.03	5.331	0.83
Average	" " "				"	116.55	99.19	17.36	....	27.06	5.391	0.84
A 94	Rolled Al-Mn alloy		"	Jan. 2, 1922	28	26.31	19.61	6.70	0.05 x1.99x5.99	24.64	9.710	1.51
A 95	" " "	Composition not	"	"	"	26.34	19.12	7.22	0.05 x1.99x5.99	24.64	10.464	1.62
A 96	" " "	furnished	"	"	"	26.64	19.33	7.31	0.05 x1.99x5.98	24.60	10.612	1.64
Average	" " "				"	26.43	19.35	7.08	....	24.63	10.262	1.59
A 97	Rolled Al alloy		"	Feb. 13, 1922	70	27.37	20.67	6.70	0.05 x2.01x6.02	25.00	3.829	0.59
A 98	" " "	Composition not	"	"	"	27.62	21.00	6.62	0.05 x2.01x6.03	25.04	3.776	0.59
A 99	" " "	furnished	"	"	"	27.63	21.04	6.59	0.05 x2.01x6.02	25.00	3.766	0.58
Average	" " "				"	27.54	20.90	6.64	....	25.01	3.790	0.59
	HIGH SILICON CAST IRON.											
A130	High silicon cast	Si 13-14	"	April 3, 1922	119	371.07	310.08	60.99	0.28 x2.00x5.94	28.21	18.168	2.82
A131	iron	Graphite 1.3	"	"	"	276.05	222.66	53.39	0.21 x2.04x5.96	27.68	16.201	2.51
A132	High silicon cast	Fe, balance	"	"	"	270.10	210.51	59.59	0.21 x2.01x5.94	27.22	18.361	2.85
Average	iron				"	305.74	247.75	57.99	....	27.70	17.577	2.72

[a] *The chemical compositions, as given, were submitted by the manufacturers and are in most instances only approximate type compositions.*

[b] *A-90 was not cleaned after removal from water, the coating was left on the test specimen for further study.*

TABLE 4.—*Composition and loss in weight of test specimens exposed to action of Montour No. 1 mine water—Concluded.*

Test piece number.	Designation.	Approximate chemical composition[a], per cent.	Date.		Days immersed.	Weight, in grams.		Loss in weight, in grams.	Dimensions of test specimens, in inches.	Area of test specimens, in square inches.	Loss in milligrams, per sq. inch per day.	Loss in milligrams, per sq. cm. per day.
			Immersed.	Removed.		Before immersion.	After immersion.					
1	2	3	4	5	6	7	8	9	10	11	12	13
	HIGH SILICON CAST IRON											
A133	High silicon cast	Si 14-14.5, P 0.16-0.20	Dec. 5, 1921	April 3, 1922	119	400.57	400.42	0.15	0.28 x2.05x5.99	29.06	0.00437	0.00067
A134	iron	C 0.2-0.6, S 0.05 max.	"	"	"	391.72	391.72	0.00	0.28 x2.02x5.98	28.64	0.00000	0.00000
A135	High silicon cast	Mn 0.35 approx.	"	"	"	401.35	401.34	0.01	0.28 x2.05x5.98	29.02	0.00292	0.00045
Average	iron	Fe, balance			"	397.88	397.83	0.05	....	28.91	0.00243	0.00037
	RUSTLESS STEELS.											
A106	Rolled high	Cr 29.5	"	"	"	97.90	97.90	0.00	0.06 x2.02x5.98	25.12	0.00000	0.00000
A107	chromium rust-	Mn 0.27, C 0.36	"	"	"	98.23	98.22	0.01	0.07 x2.01x5.98	25.16	0.00336	0.00052
A108	less steel	Si 0.53	"	"	"	96.66	96.65	0.01	0.07 x2.05x5.99	25.69	0.00330	0.00050
Average		Fe, balance			"	97.60	97.59	0.01	....	25.32	0.00220	0.00031
A100	Rolled rustless		"	"	"	99.56	99.55	0.01	0.065x2.02x5.95	25.08	0.0033	0.00051
A101	steel "A"	Highly alloyed	"	"	"	97.84	97.83	0.01	0.065x2.01x6.00	25.16	0.0033	0.00051
A102	Rolled rustless	Cr-Ni-Si steel	"	"	"	97.00	96.99	0.01	0.065x1.98x5.99	24.76	0.0034	0.00052
Average	steel "A"				"	97.97	97.96	0.01	....	25.00	0.0033	0.00051
A103	Rolled rustless		"	"	"	106.34	105.39	0.95	0.07 x2.04x6.04	25.77	0.309	0.048
A104	steel "B"	Highly alloyed	"	"	"	109.01	108.24	0.77	0.07 x2.02x6.01	25.40	0.255	0.040
A105	Rolled rustless	Cr-Ni-Si steel	"	"	"	105.36	105.27	0.09	0.07 x2.00x6.00	25.12	0.030	0.047
Average	steel "B"				"	106.90	106.30	0.60	....	25.43	0.122	0.045
	MISCELLANEOUS METALS, ALLOYS.											
	METALS.											
A115	Rolled pure ingot	Fe 99.9	"	Jan. 16, 1922	42	79.81	57.09	22.72	0.05 x2.01x6.11	25.87	21.821	3.30
A116	iron		"	"	"	78.01	56.63	21.38	0.05 x2.00x6.09	25.17	20.223	3.13
A117	Rolled pure ingot		"	"	"	79.47	52.57	26.90	0.05 x2.01x6.10	25.88	25.280	3.92
Average	iron				"	79.10	55.43	23.67	....	25.29	22.275	3.45

A109	Rolled pure		"	Jan. 2, 1922	28	26.55	22.73	3.82	0.05 x1.99x6.01	24.72	5.518	0.86
A110	aluminum........	Pure aluminum.......	"	"	"	26.93	23.17	3.76	0.05 x1.99x6.01	24.72	5.482	0.84
A111	Rolled pure		"	"	"	26.36	22.65	3.71	0.05 x1.99x6.01	24.72	5.357	0.83
Average	aluminum........				"	26.61	22.85	3.76	....	24.72	5.436	0.84
A 25	Rolled pure copper		"	April 3, 1922	119	92.74	56.44	36.30	0.053x2.03x6.00	25.21	12.092	1.87
A 26	" " "	Pure copper.........	"	"	"	93.71	57.28	36.43	0.053x2.02x6.00	25.09	12.193	1.89
A 27	" " "		"	"	"	92.32	55.81	36.51	0.052x2.02x6.00	25.07	12.235	1.90
Average	" " "				"	92.92	56.51	36.41	....	25.12	12.173	1.89
A121	Rolled nickel......		"	"	"	86.75	59.12	27.63	0.05 x2.00x6.06	25.05	9.268	1.44
A122	" "	Ni 99.0..............	"	"	"	86.68	58.92	27.76	0.05 x2.00x6.05	25.01	9.663	1.50
A123	" "		"	"	"	86.68	58.80	27.88	0.05 x2.00x6.04	24.96	9.385	1.45
Average	" "				"	86.70	58.95	27.76	....	25.01	9.439	1.46
	ALLOYS.											
A 76	Cast aluminum		"	"	"	249.98	231.94	18.04	0.19 x1.90x5.88	25.30	5.991	0.93
A 77	bronze..........	Cu 90...............	"	"	"	251.10	234.23	16.87	0.19 x1.90x5.88	25.30	5.603	0.87
A 78	Cast aluminum	Al 10...............	"	"	"	250.00	232.69	17.31	0.19 x1.90x5.87	25.25	5.760	0.89
Average	bronze..........				"	250.36	232.95	17.41	....	25.28	5.785	0.90
A 52	Rolled iron	Cu 85...............	"	"	"	99.61	69.51	30.10	0.07 x2.00x5.98	25.10	10.075	1.56
A 53	aluminum bronze...	Fe 8...............	"	"	"	97.94	69.04	28.90	0.07 x1.99x5.99	25.02	9.705	1.50
A 54	Rolled iron	Al 7...............	"	"	"	92.04	64.66	27.38	0.06 x2.01x5.99	25.04	9.184	1.42
Average	aluminum bronze..				"	96.53	67.74	28.79	....	25.05	9.655	1.50
A 70	Cast Cu-Pb alloy..		"	"	"	460.91	450.84	10.07	0.25 x1.90x6.00	26.75	3.163	0.49
A 71	" " " ..	Cu 50...............	"	"	"	464.47	453.82	10.65	0.25 x1.90x6.00	26.75	3.345	0.52
A 72	" " " ..	Pb 50...............	"	"	"	463.48	454.43	9.05	0.25 x1.91x6.00	26.88	2.828	0.44
Average	" " " ..				"	462.95	453.03	9.92	....	26.79	3.112	0.48
A 40	Rolled monel metal	Ni 67.0, Cu 28 ..	"	"	"	114.79	86.71	28.08	0.063x2.05x5.98	25.53	9.242	1.43
A 41	" " "	Mn 1.75, Fe 1.76..	"	"	"	115.81	89.44	26.37	0.063x2.05x6.06	25.87	8.563	1.33
A 42	" " "	C 0.2, Si 0.18..	"	"	"	113.01	86.79	26.22	0.064x2.05x6.02	25.71	8.563	1.33
Average	" " "	S 0.026 ..			"	114.54	87.65	26.89	....	25.70	8.789	1.36
A 61	Rolled Cu-Mn-Fe	Cu 95...............	"	"	"	87.91	51.68	36.23	0.05 x2.01x6.02	25.00	12.176	1.89
A 62	alloy............	Mn 4...............	"	"	"	85.20	49.74	35.46	0.05 x2.01x6.02	25.00	11.915	1.85
A 63	Rolled Cu-Mn-Fe	Fe 1...............	"	"	"	88.56	52.97	35.59	0.05 x2.01x6.02	25.00	11.957	1.85
Average	alloy............				"	87.22	51.46	35.76	....	25.00	12.016	1.86
A118	Rolled nichrome...	Ni 58-62 ..	"	"	"	80.28	78.88	1.40	0.05 x2.00x6.06	25.05	0.4695	0.07277
A119	" " ...	Cr 12-14 ..	"	"	"	78.13	78.10	.03	0.05 x2.00x6.04	24.96	0.0012	0.00018
A120	" " ...	Fe 25, Mn 1.25-1.50..	"	"	"	79.29	79.20	.09	0.05 x2.00x6.06	25.05	0.0030	0.00047
Average	" " ...	Si 0.5 ..			"	79.23	78.73	.51	....	25.02	0.1580	0.02454

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[a] *The chemical compositions, as given, were submitted by the manufacturers and are in most instances only approximate type compositions.*

TABLE 5.—*Composition and loss in weight of test specimens exposed to action of Edna No. 2 mine water.*

Test piece number.	Designation.	Approximate chemical composition[a], per cent.	Date.		Days immersed.	Weight, in grams.		Loss in weight, in grams.	Dimensions of test specimens, in inches.	Area of test specimens, in square inches.	Loss in milligrams, per sq. inch per day.	Loss in milligrams, per sq. cm. per day.
			Immersed.	Removed.		Before immersion.	After immersion.					
1	2	3	4	5	6	7	8	9	10	11	12	13
	BRASSES.											
B 16	Rolled high brass..		Nov. 15, 1922	Jan. 19, 1922	65	86.94	10.18	76.76	0.05 x2.00x6.00	24.80	47.616	7.38
B 17	" " " ..	Cu 66.6...........	"	"	"	85.20	10.18	75.02	0.05 x2.00x5.99	24.76	46.612	7.22
B 18	" " " ..	Zn 33.4............	"	"	"	85.97	11.00	74.97	0.05 x2.00x6.00	24.80	46.506	7.21
Average	" " " ..				"	86.04	10.45	75.58	....	24.79	46.913	7.27
B 19	Rolled low brass..		"	"	"	86.15	11.83	74.32	0.05 x2.00x6.04	24.96	45.807	7.10
B 20	" " " ..	Cu 80...............	"	"	"	86.43	11.26	75.17	0.05 x2.00x6.04	24.96	46.332	7.18
B 21	" " " ..	Zn 20...............	"	"	"	86.21	11.21	75.00	0.05 x2.00x6.04	24.96	46.227	7.16
Average	" " " ..				"	86.26	11.43	74.83	....	24.96	46.122	7.15
B 22	Rolled Naval brass	Cu 60.4.............	"	"	"	81.71	00.00	81.71	0.049x2.00x6.00	24.78	50.729	7.86
B 23	" " "	Zn 38.8.............	"	"	"	86.60	13.43	73.17	0.052x2.00x6.00	24.83	45.335	7.03
B 24	" " "	Sn 0.8.............	"	"	"	86.57	19.54	67.03	0.052x2.00x5.99	24.79	41.598	6.45
Average	" " "				"	84.96	10.99	73.97	....	24.80	45.887	7.11
B 28	Rolled brass		"	"	"	86.74	12.62	74.12	0.05 x2.01x6.01	24.96	45.684	7.08
B 29	(Admiralty metal),	Cu 70, Sn 1...........	"	"	"	85.91	12.22	73.69	0.051x2.01x5.99	24.90	45.529	7.06
B 30	grain size	Zn 29	"	"	"	86.53	12.43	74.10	0.05 x2.01x6.02	25.00	45.600	7.07
Average	0.025 mm.........				"	86.39	12.42	73.97	....	24.95	45.604	7.07
B 64[b]	Rolled brass		"	Dec. 20, 1921	35	87.69	55.21	32.48	0.052x2.01x6.02	25.04	37.060	5.74
B 65	(Admiralty metal),	Cu 70, Zn 29.........	"	Jan. 19, 1922	65	88.59	15.93	72.66	0.052x2.01x6.02	25.04	44.641	6.92
B 66	grain size	Sn 1	"	"	"	86.36	16.16	70.20	0.052x2.01x6.02	25.04	43.130	6.68
Average	0.035 mm.........				55	87.55	29.10	58.44	....	25.04	41.610	6.45
B 67[b]	Rolled brass		"	Dec. 20, 1921	35	86.94	53.04	33.90	0.052x2.01x6.03	25.08	38.617	5.98
B 68	(Admiralty metal),	Cu 70, Zn 29.........	"	Jan. 19, 1922	65	86.81	15.54	71.27	0.052x2.01x6.03	25.08	43.718	6.78
B 69	grain size	Sn 1	"	"	"	88.81	18.76	70.05	0.054x2.01x6.02	25.07	42.986	6.66
Average	0.075 mm.........				55	87.52	29.11	58.41	....	25.08	41.774	6.47

B 46	Rolled manganese	Cu 57-60, Zn 37-40	"	Jan. 26, 1922	72	109.10	25.71	83.39	0.065x2.02x6.03	25.41	45.579	7.06
B 47	bronze	Sn 0.5-1.5, Fe 0.8-2,	"	"	"	116.17	36.62	79.55	0.07 x2.02x6.04	25.53	43.276	6.71
B 48	Rolled manganese	Mn 0.3 (maximum)	"	"	"	117.12	42.60	74.52	0.07 x2.03x6.03	25.61	40.413	6.26
Average	bronze	Pb 0.2 (maximum)			"	114.13	34.98	79.15		25.52	43.089	6.67
	BRONZES.											
B 79	Cast bronze		"	Mar. 30, 1922	135	318.24	274.99	43.25	0.19 x1.96x5.97	26.10	12.274	1.90
B 80	" "	Cu 90	"	"	"	317.26	262.75	54.51	0.19 x1.96x5.97	26.10	15.470	2.40
B 81	" "	Sn 10	"	"	"	318.94	272.38	46.56	0.19 x1.96x5.97	26.10	13.214	2.05
Average	" "				"	318.15	270.04	48.11		26.10	13.653	2.12
B 55[b]	Rolled bronze		"	Dec. 20, 1921	35	86.76	53.16	33.60	0.05 x2.01x6.02	25.00	38.400	5.95
B 56	" "	Cu 98.7	"	Jan. 19, 1922	65	86.78	13.43	73.35	0.05 x2.01x6.02	25.00	45.138	6.99
B 57	" "	Sn 1.3	"	"	"	85.55	11.40	74.25	0.05 x2.01x6.02	25.00	45.692	7.08
Average	" "				55	86.40	26.00	60.40		25.00	43.076	6.68
B 58	Rolled phosphor	Cu 94.4	"	Feb. 2, 1922	79	90.10	26.47	63.63	0.05 x2.01x6.02	25.00	32.217	4.99
B 59	bronze	Sn 5.5	"	"	"	91.31	34.79	56.52	0.05 x2.01x6.02	25.00	28.617	4.43
B 60	Rolled phosphor	P 0.1	"	"	"	91.78	32.86	58.92	0.05 x2.01x6.02	25.00	29.832	4.62
Average	bronze				"	91.06	31.37	59.69		25.00	30.222	4.68
B 49	Rolled zinc	Cu 85-90, Zn 4 max.	"	Mar. 30, 1922	135	110.95	65.96	44.99	0.06 x2.01x6.00	25.08	13.287	2.06
B 50	phosphor bronze	Sn 6-11, Pb 0.2 max.	"	"	"	110.58	78.84	31.74	0.06 x2.01x6.00	25.08	9.374	1.45
B 51	Rolled zinc	P 0.5 max.	"	"	"	110.96	76.13	34.83	0.06 x2.01x6.02	25.16	10.254	1.59
Average	phosphor bronze				"	110.83	73.64	37.19		25.11	10.971	1.70
B 73	Cast leaded zinc		"	"	"	341.78	323.95	17.83	0.21 x1.96x5.98	26.77	4.934	0.76
B 74	bronze	Cu 86, Pb 0.5	"	"	"	338.89	318.17	20.72	0.21 x1.96x5.98	26.77	5.733	0.89
B 75	Cast leaded zinc	Sn 12, Zn 1.5	"	"	"	343.36	323.58	19.78	0.21 x1.96x5.98	26.77	5.473	0.85
Average	bronze				"	341.34	321.90	19.44		26.77	5.380	0.83
B 85[b]	Cast leaded bronze	Cu 75	"	Dec. 20, 1921	35	411.95	403.56	8.39	0.25 x1.97x6.00	27.63	8.676	1.34
B 86	" " "	Sn 10	"	Mar. 30, 1922	135	401.92	371.19	30.73	0.24 x1.97x6.00	27.47	8.286	1.28
B 87	" " "	Pb 15	"	"	"	417.43	389.87	27.56	0.25 x1.97x6.00	27.63	7.389	1.15
Average	" " "				102	410.43	388.21	22.23		27.58	8.117	1.26
B 82	Cast leaded bronze	Cu 88.1	"	"	135	381.34	310.43	70.91	0.22 x1.98x5.95	27.05	19.417	3.01
B 83	" " "	Sn 9.9	"	"	"	379.86	321.11	58.75	0.22 x1.98x5.95	27.05	16.088	2.49
B 84	" " "	Pb 2.0	"	"	"	382.16	330.94	51.22	0.22 x1.98x5.95	27.05	14.025	2.17
Average	" " "				"	381.12	320.83	60.29		27.05	16.510	2.56
	CUPRO-NICKEL.											
B 37	Rolled cupro-nickel		"	Jan. 19, 1922	65	88.88	11.63	77.25	0.05 x2.01x6.00	24.92	47.690	7.39
B 38	(coin metal)	Cu 75	"	"	"	89.28	13.06	76.22	0.05 x2.01x6.01	24.96	46.978	7.28
B 39	Rolled cupro-nickel	Ni 25	"	"	"	89.46	12.38	77.08	0.05 x2.01x6.02	25.00	47.433	7.35
Average	(coin metal)				"	89.21	12.36	76.85		24.96	47.367	7.34

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[a] *The chemical compositions, as given, were submitted by the manufacturers and are in most instances only approximate type compositions.*

[b] *This test specimen was removed for study.*

TABLE 5.—*Composition and loss in weight of test specimens exposed to action of Edna No. 2 mine water—Continued.*

Test piece number.	Designation.	Approximate chemical composition[a], per cent.	Date.		Days immersed.	Weight, in grams.		Loss in weight, in grams.	Dimensions of test specimens, in inches.	Area of test specimens, in square inches.	Loss in milligrams, per sq. inch per day.	Loss in milligrams, per sq. cm. per day.
			Immersed.	Removed.		Before immersion.	After immersion.					
1	2	3	4	5	6	7	8	9	10	11	12	13
	CUPRO-NICKEL.											
B 31	Rolled cupro-nickel		Nov. 15, 1921	Jan. 19, 1922	65	85.20	6.88	78.32	0.047x2.01x6.03	25.00	48.196	7.47
B 32	" " "	Cu 85..............	"	"	"	84.82	7.22	77.60	0.047x2.01x6.02	24.95	47.849	7.42
B 33	" " "	Ni 15..............	"	"	"	83.89	5.13	78.76	0.047x2.01x6.03	25.00	48.467	7.51
Average	" " "				"	84.64	6.41	78.23	....	24.98	48.171	7.46
B 1	Cast leaded cupro-	Cu 50-60............	"	Mar. 30, 1922	135	597.65	493.79	103.86	0.33 x1.96x6.00	28.77	26.720	4.14
B 2	nickel............	Ni 20-30............	"	"	"	601.38	505.94	95.44	0.33 x1.96x6.00	28.77	24.554	3.80
B 3	Cast leaded cupro-	Pb 20-30............	"	"	"	601.49	494.07	107.42	0.34 x1.96x6.01	28.99	27.424	4.25
Average	nickel............				"	600.17	497.93	102.24	....	28.84	26.233	4.06
B 4	Cast chromium-	Cu 35-45, Fe 12-20...	"	"	"	515.83	346.96	168.87	0.34 x1.91x5.97	28.17	44.371	6.88
B 5	iron cupro-nickel..	Ni 35-45 ...	"	"	"	516.27	353.44	162.83	0.34 x1.91x5.97	28.17	42.784	6.63
B 6	Cast chromium-	Ferro-Chromium 6-16	"	"	"	530.88	370.59	160.29	0.34 x1.91x5.97	28.17	42.116	6.53
Average	iron cupro-nickel..				"	520.99	356.99	164.00	....	28.17	43.090	6.68
B112[b]	Cast iron man-	Cu 75..............	"	Dec. 20, 1921	35	215.86	182.33	33.53	0.12 x1.99x6.00	25.80	37.180	5.76
B113	ganese cupro-	Ni 15..............	"	Mar. 30, 1922	135	204.94	41.66	163.28	0.12 x1.99x6.00	25.80	46.878	7.27
B114	nickel............	Fe and Mn, balance....	"	Mar. 16, 1922	121	206.14	56.05	150.09	0.12 x1.99x6.01	25.84	48.003	7.44
Average					97	208.98	93.35	115.63	....	25.81	44.004	6.82
	NICKEL SILVER.											
B 13	Rolled nickel silver	Cu 63.8............	"	Jan. 19, 1922	65	87.56	12.44	75.12	0.05 x2.01x6.04	25.09	46.061	7.14
B 14	" " "	Zn 17.7............	"	"	"	87.60	15.07	72.53	0.05 x2.01x6.04	25.09	44.472	6.89
B 15	" " "	Ni 18.5............	"	"	"	86.76	11.19	75.57	0.05 x2.01x6.04	25.09	46.336	7.18
Average	" " "				"	87.31	12.90	74.41	....	25.09	45.623	7.07
B 43	Rolled iron nickel		"	"	"	91.14	9.45	81.69	0.053x1.99x6.08	24.85	50.573	7.84
B 44	silver............	Cu 60-70, Ni 9-15....	"	Jan. 5, 1922	51	89.18	30.11	59.02	0.052x1.99x6.04	24.88	46.511	7.21
B 45	Rolled iron nickel	Zn 20-25, Fe 1- 4....	"	Jan. 19, 1922	65	88.29	11.95	76.34	0.052x2.00x6.03	24.96	47.052	7.29
Average	silver...........				60	89.52	17.17	72.35	....	24.90	48.045	7.45

B 34	Rolled nickel silver	Cu 52	“	Jan. 19, 1922	65	83.26	7.41	75.85	0.05 x2.00x6.00	24.80	47.052	7.29
B 35	“ “ “	Zn 36	“	“	“	83.47	9.07	74.40	0.05 x2.00x6.00	24.80	46.153	7.15
B 36	“ “ “	Ni 12	“	“	“	82.31	6.66	75.65	0.05 x2.00x6.00	24.80	46.929	7.27
Average	“ “ “				“	83.01	7.71	75.30	....	24.80	46.711	7.24
B 10	Cast silicon nickel silver		“	Mar. 30, 1922	135	197.05	39.04	158.01	0.12 x1.96x6.00	25.43	46.025	7.13
B 11		Cu 49, Zn 25	“	“	“	192.87	36.12	156.75	0.12 x1.97x6.00	25.55	45.444	7.04
B 12	Cast silicon nickel silver	Ni 25, Si 1	“	“	“	191.17	36.05	155.12	0.12 x1.98x6.00	25.68	44.743	6.93
Average					“	193.70	37.07	156.63	....	25.55	45.404	7.04
B 7	Cast tin-lead nickel silver	Cu 60, Zn 14	“	“	“	374.37	274.29	100.08	0.22 x1.95x5.99	26.85	27.589	4.27
B 8		Ni 15, Pb 8	“	“	“	376.43	277.69	98.74	0.22 x1.95x5.99	26.85	27.237	4.22
B 9	Cast tin-lead nickel silver	Sn 3	“	“	“	376.63	279.30	97.33	0.22 x1.95x5.99	26.85	26.851	4.16
Average					“	375.81	277.09	98.72	....	26.85	27.226	4.22
B136	Cast tin-lead nickel silver	Cu 57, Ni 19.5	Feb. 2, 1922	“	56	440.75	391.68	49.07	0.26 x2.00x5.98	28.07	31.216	4.84
B137		Sn 2, Zn 16	“	“	“	443.99	399.69	44.30	0.26 x2.00x5.99	28.11	28.141	4.36
B138	Cast tin-lead nickel silver	Pb 6	“	“	“	445.36	402.52	42.84	0.26 x2.00x6.00	28.16	27.166	4.21
Average					“	443.37	397.96	45.40	....	28.11	28.841	4.47
	ALUMINUM ALLOYS.											
B 88	Cast Al-Si alloy...		Nov. 15, 1921	Jan. 26, 1922	72	118.07	90.19	27.88	0.23 x1.98x5.99	27.39	14.186	2.19
B 89	“ “ “ ...	Al 95	“	“	“	117.90	89.58	28.32	0.23 x1.98x5.99	27.39	14.359	2.23
B 90	“ “ “ ...	Si 5	“	“	“	118.35	90.74	27.61	0.23 x1.98x5.99	27.39	14.004	2.17
Average	“ “ “ ...				“	118.11	90.17	27.94	....	27.39	14.166	2.20
B 91	Cast Al-Mn alloy..		“	“	“	116.29	88.27	28.02	0.23 x1.98x5.92	27.07	14.376	2.23
B 92	“ “ “ ..	Al 98	“	“	“	115.76	87.72	28.04	0.23 x1.98x5.92	27.07	14.386	2.23
B 93	“ “ “ ..	Mn 2	“	“	“	115.93	88.04	27.89	0.23 x1.98x5.92	27.07	14.308	2.22
Average	“ “ “ ..				“	115.99	88.01	27.98	....	27.07	14.357	2.23
B 94[b]	Rolled Al-Mn alloy		“	Nov. 22, 1921	7	25.95	23.01	2.94	0.05 x1.99x5.98	24.60	17.072	2.64
B 95	“ “ “	Composition not furnished	“	Dec. 6, 1921	21	26.33	20.73	5.60	0.05 x1.99x5.98	24.60	10.840	1.68
B 96	“ “ “		“	“	“	26.38	20.46	5.92	0.05 x1.99x5.98	24.60	11.459	1.78
Average	“ “ “				16	26.22	21.40	4.82	....	24.60	13.124	2.03
B 97	Rolled Al alloy....		“	Jan. 5, 1922	51	27.49	12.49	15.00	0.05 x2.01x6.02	25.00	11.764	1.82
B 98	“ “ “	Composition not furnished	“	“	“	27.53	13.32	14.21	0.05 x2.01x6.02	25.00	11.145	1.72
B 99	“ “ “		“	“	“	27.53	13.17	14.36	0.05 x2.01x6.02	25.00	11.262	1.74
Average	“ “ “				“	27.52	12.99	14.52	....	25.00	11.390	1.76
	HIGH SILICON CAST IRON.											
B130	High silicon cast iron	Si 13-14	“	Mar. 30, 1922	135	275.36	261.06	14.30	0.21 x2.00x5.97	27.23	3.890	0.60
B131		Graphite, 1.3	“	“	“	364.62	350.20	14.42	0.28 x2.00x5.92	28.12	3.799	0.59
B132[b]	High silicon cast iron	Fe, balance	“	Dec. 20, 1921	35	271.00	189.33	81.67	0.21 x1.99x5.91	26.84	86.937	13.48
Average					102	303.66	266.86	36.80	....	27.40	31.539	4.89

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[a] *The chemical compositions, as given, were submitted by the manufacturers and are in most instances only approximate type compositions.*

[b] *This test specimen was removed for study.*

TABLE 5.—*Composition and loss in weight of test specimens exposed to action of Edna No. 2 mine water—Concluded.*

Test piece number.	Designation.	Approximate chemical composition[a], per cent.	Date.		Days immersed.	Weight, in grams.		Loss in weight, in grams.	Dimensions of test specimens, in inches.	Area of test specimens, in square inches.	Loss in milligrams, per sq. inch per day.	Loss in milligrams, per sq. cm. per day.
			Immersed.	Removed.		Before immersion.	After immersion.					
1	2	3	4	5	6	7	8	9	10	11	12	13
	HIGH SILICON CAST IRON											
B133	High silicon cast	Si 14-14.5, P 0.16-0.20	Nov. 15, 1921	Mar. 30, 1922	135	295.54	295.41	0.13	0.21 x2.02x6.00	27.61	0.03487	0.00540
B134	iron............	C 0.2-0.6, S .05 max.	"	"	"	293.52	293.38	0.14	0.21 x2.02x5.99	27.56	0.03763	0.00582
B135	High silicon cast	Mn 0.35 (approximate)	"	"	"	417.65	417.65	0.00	0.30 x2.02x5.96	28.87	0.00000	0.00000
Average	iron............	Fe, balance..........			"	335.57	335.48	0.09	....	28.00	0.02416	0.00374
	RUSTLESS STEEL.											
B106	Rolled high	Cr 29.5, Mn 0.27....	"	"	"	98.53	98.52	0.01	0.07 x2.01x6.03	25.37	0.00291	0.00045
B107	chromium rust-	C 0.36, Si 0.53....	"	"	"	97.08	97.07	0.01	0.07 x2.01x6.01	25.28	0.00293	0.00045
B108	less steel........	Fe, balance..........	"	"	"	95.88	95.88	0.00	0.07 x2.01x6.00	25.24	0.00000	0.00000
Average					"	97.16	97.15	0.01	....	25.30	0.00195	0.00030
B100	Rolled rustless		"	"	"	97.31	97.30	0.01	0.062x2.02x6.00	25.23	0.00293	0.00045
B101	steel "A"........	Highly alloyed	"	"	"	98.51	98.51	0.00	0.065x2.02x5.97	25.16	0.00000	0.00000
B102	Rolled rustless	Cr-Ni-Si steel........	"	"	"	100.60	100.60	0.00	0.065x2.02x6.06	25.65	0.00000	0.00000
Average	steel "A"........				"	98.81	98.80	0.01	....	25.35	0.00094	0.00015
B103	Rolled rustless		"	"	"	106.18	106.16	0.02	0.065x2.04x6.03	25.65	0.00577	0.00089
B104	steel "B"........	Highly alloyed	"	"	"	104.24	104.24	0.00	0.07 x2.00x6.05	25.35	0.00000	0.00000
B105	Rolled rustless	Cr-Ni-Si steel........	"	"	"	106.58	106.55	0.03	0.07 x2.02x6.04	25.53	0.00870	0.00134
Average	steel "B"........				"	105.67	105.65	0.02	....	25.50	0.00480	0.00074
	MISCELLANEOUS METALS AND ALLOYS.											
	METALS.											
B115	Rolled pure ingot		"	Dec. 20, 1921	35	79.92	40.48	39.44	0.05 x2.01x6.10	25.33	44.485	6.89
B116	iron............	Fe 99.9............	"	"	"	79.79	39.98	39.81	0.05 x2.00x6.09	25.17	45.188	7.01
B117	Rolled pure ingot		"	"	"	79.60	36.49	43.11	0.05 x2.01x6.11	25.37	48.548	7.58
Average	iron............				"	79.77	38.98	40.79	....	25.29	46.074	7.14

B109	Rolled pure	Pure aluminum.......	"	Dec. 6, 1921	21	26.80	21.62	5.18	0.05 x1.99x6.00	24.68	9.993	1.55
B110	aluminum.........		"	"	"	26.89	21.78	5.11	0.05 x1.99x6.01	24.72	9.843	1.53
B111	Rolled pure		"	"	"	26.63	21.36	5.27	0.05 x1.99x6.01	24.72	10.151	1.57
Average	aluminum.........				"	26.77	21.59	5.19	....	24.71	9.956	1.55
B 25[b]	Rolled pure copper	Pure copper.........	"	Dec. 20, 1921	35	94.46	59.17	35.29	0.053x2.02x6.00	25.09	40.185	6.23
B 26	" " "		"	Jan. 19, 1922	65	93.46	15.41	78.05	0.055x2.02x6.01	25.16	47.724	7.40
B 27	" " "		"	"	"	94.10	14.77	79.33	0.053x2.02x6.00	25.09	48.643	7.53
Average	" " "				33	94.01	29.78	64.22	....	25.11	45.517	7.06
B122	Rolled nickel......	Ni 99...............	"	Mar. 30, 1922	135	86.54	85.94	0.60	0.05 x2.00x6.04	24.94	0.01782	0.00276
B123	" "		"	"	"	86.55	85.85	0.70	0.05 x2.00x6.04	24.94	0.02079	0.00322
Average	" "				"	86.54	85.89	0.65	....	24.94	0.01930	0.00299
	ALLOYS.											
B 76	Cast aluminum		"	"	"	254.15	141.19	112.96	0.19 x1.90x5.87	25.25	33.137	5.14
B 77	bronze...........	Cu 90...............	"	"	"	234.65	119.43	115.22	0.20 x1.93x5.93	26.03	32.788	5.08
B 78	Cast aluminum	Al 10...............	"	"	"	250.73	139.91	110.82	0.19 x1.90x5.87	25.25	32.510	5.04
Average	bronze...........				"	246.51	133.51	113.00	....	25.51	32.812	5.08
B 52	Rolled iron	Cu 85...............	"	Feb. 16, 1922	93	125.23	30.95	94.28	0.08 x2.02x5.98	25.44	39.848	6.18
B 53	aluminum bronze..	Fe 8...............	"	Jan. 26, 1922	72	94.85	24.18	70.67	0.07 x2.00x5.99	25.08	39.134	6.06
B 54	Rolled iron	Al 7...............	"	"	"	102.30	34.32	67.98	0.07 x2.01x5.99	25.20	37.466	5.81
Average	aluminum bronze..				86	107.46	29.82	77.64	....	25.24	38.861	6.02
B 70[b]	Cast Cu-Pb alloy.		Nov. 29, 1921	Dec. 20, 1921	21	457.97	441.67	16.30	0.25 x1.91x6.00	26.88	28.875	4.47
B 71	" " " ..	Cu 50...............	"	Mar. 30, 1922	121	464.34	382.01	82.33	0.25 x1.90x6.00	26.75	25.435	3.94
B 72	" " " ..	Pb 50...............	"	"	"	463.79	396.59	67.20	0.25 x1.91x6.00	26.88	20.661	3.20
Average	" " " ..				88	462.03	406.76	55.28	....	26.84	24.990	3.87
B 40	Rolled monel metal	Ni 67.0, Cu 28 ..	Nov. 15, 1921	Feb. 2, 1922	79	111.38	23.86	87.52	0.064x2.01x6.03	25.27	43.839	6.70
B 41	" " "	Mn 1.75, Fe 1.76..	"	"	"	107.13	23.80	83.33	0.062x1.95x6.06	24.62	42.843	6.64
B 42	" " "	C 0.2, Si 0.18..	"	"	"	114.46	28.46	86.00	0.065x1.98x6.06	25.05	43.456	6.73
Average	" " "	S 0.026 ..			"	110.99	25.37	85.62	....	24.98	43.379	6.72
B 61	Rolled Cu-Mn-Fe	Cu 95...............	"	Jan. 19, 1922	65	87.76	10.71	77.05	0.05 x2.01x6.02	25.00	47.415	7.34
B 62	alloy............	Mn 4...............	"	"	"	89.04	11.30	77.74	0.05 x2.01x6.02	25.00	47.840	7.42
B 63	Rolled Cu-Mn-Fe	Fe 1...............	"	"	"	87.33	9.88	77.45	0.05 x2.01x6.02	25.00	47.661	7.39
Average	alloy............				"	88.04	10.63	77.41	....	25.00	47.639	7.38
B139	Rolled Ni-Cr-Fe	Ni 65, Cr 16	Feb. 16, 1922	Mar. 30, 1922	42	51.87	26.42	25.42	0.067x1.01x5.99	13.04	46.466	7.20
B140	alloy............	Mn 0.7, Si 0.7....	"	"	"	51.46	24.96	26.50	0.067x1.01x5.98	13.02	48.459	7.51
B141	Rolled Ni-Cr-Fe	Al 0.15, Fe, balance.	"	"	"	51.68	24.90	26.78	0.067x1.01x5.96	12.97	49.326	7.64
Average	alloy............				"	51.67	25.43	26.24	....	13.01	48.084	7.45
B118	Rolled nichrome...	Ni 58-62...........	Nov. 15, 1921	"	135	80.51	79.44	1.07	0.05 x1.99x6.04	24.84	0.31891	0.04942
B119	" " ...	Cr 12-14...........	"	"	"	77.87	77.83	0.04	0.05 x1.99x6.05	24.88	0.01190	0.00184
B120	" " ...	Fe 25, Mn 1.25-1.50	"	"	"	77.44	77.37	0.07	0.05 x1.99x6.02	24.76	0.02094	0.00324
Average	" " ...	Si 0.5............			"	78.61	78.21	0.39	....	24.83	0.11725	0.01816

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[a] *The chemical compositions, as given, were submitted by the manufacturers and are in most instances only approximate type compositions.*

[b] *This test specimen was removed for study.*

TABLE 6.—*Composition and loss in weight of test specimens exposed to action of Calumet mine water*

Test piece number.	Designation.	Approximate chemical composition[a], per cent.	Date.		Days immersed.	Weight, in grams.		Loss in weight, in grams.	Dimensions of test specimens, in inches.	Area of test specimens, in square inches.	Loss in milligrams, per sq. inch per day.	Loss in milligrams, per sq. cm. per day.
			Immersed.	Removed.		Before immersion.	After immersion.					
1	2	3	4	5	6	7	8	9	10	11	12	13
	BRASSES.											
C 16	Rolled high brass.		Dec. 20, 1921	Mar. 30, 1922	98[b]	86.00	64.78	21.22	0.05 x 2.00 x 6.00	24.80	8.731	1.85
C 17	" " " ..	Cu 66.6............	"	"	"	86.42	63.82	22.60	0.05 x 2.00 x 6.00	24.80	9.298	1.44
C 18	" " " ..	Zn 33.4............	"	"	"	86.36	63.38	22.98	0.05 x 2.00 x 6.00	24.80	9.455	1.46
Average	" " " ..				"	86.26	63.99	22.23	....	24.80	9.161	1.42
C 19	Rolled low brass.		"	"	"	85.19	63.20	21.99	0.05 x 2.00 x 6.04	24.96	8.989	1.39
C 20	" " " ..	Cu 80..............	"	"	"	86.94	65.19	21.75	0.05 x 2.00 x 6.04	24.96	8.891	1.38
C 21	" " " ..	Zn 20..............	"	"	"	86.57	64.33	22.24	0.05 x 2.00 x 6.04	24.96	9.092	1.41
Average	" " " ..				"	86.23	64.23	22.00	....	24.96	8.991	1.39
C 22	Rolled Naval brass	Cu 60.4............	"	"	"	80.97	59.05	21.92	0.049 x 2.00 x 6.01	24.83	9.008	1.40
C 23	" " "	Zn 38.8............	"	"	"	82.66	61.30	21.36	0.05 x 2.00 x 5.99	24.76	8.802	1.36
C 24	" " "	Sn 0.8.............	"	"	"	85.43	63.24	22.19	0.051 x 2.00 x 6.00	24.82	9.112	1.41
Average	" " "				"	83.02	61.20	21.82	....	24.80	8.974	1.39
C 28	Rolled brass (Admiralty metal), grain size 0.025 mm.........		"	"	"	87.37	70.23	17.14	0.05 x 2.01 x 6.01	24.96	7.006	1.08
C 29		Cu 70, Sn 1..........	"	"	"	87.18	69.70	17.48	0.05 x 2.01 x 6.01	24.96	7.146	1.11
C 30		Zn 29	"	"	"	87.15	69.86	17.29	0.05 x 2.01 x 6.01	24.96	7.068	1.09
Average					"	87.23	69.93	17.30	....	24.96	7.073	1.09
C 64	Rolled brass (Admiralty metal), grain size 0.035 mm.........		"	"	"	87.76	73.07	14.69	0.052 x 2.01 x 6.02	25.04	5.986	0.93
C 65		Cu 70, Sn 1...........	"	"	"	87.18	72.99	14.19	0.052 x 2.01 x 6.02	25.04	5.782	0.90
C 66		Zn 29	"	"	"	87.14	73.19	13.95	0.052 x 2.01 x 6.01	24.99	5.696	0.88
Average					"	87.36	73.08	14.28	....	25.02	5.821	0.90
C 67	Rolled brass (Admiralty metal), grain size 0.075 mm........		"	"	"	86.93	74.35	12.58	0.051 x 2.01 x 6.03	25.07	5.120	0.79
C 68		Cu 70, Sn 1...........	"	"	"	86.64	73.93	12.71	0.051 x 2.01 x 6.02	25.02	5.183	0.80
C 69		Zn 29	"	"	"	86.85	74.55	12.30	0.051 x 2.01 x 6.02	25.02	5.016	0.78
Average					"	86.81	74.28	12.53	....	25.04	5.106	0.79

C 46	Rolled manganese	Cu 57-60, Zn 37-40....	"	"	"	117.78	94.88	22.90	0.072 x 2.03 x 6.03	25.64	9.113	1.41
C 47	bronze..........	Sn 0.5-1.5, Fe 0.8-2,	"	"	"	116.77	94.16	22.61	0.07 x 2.02 x 6.08	25.49	9.051	1.40
C 48	Rolled manganese	Mn 0.8 (maximum)....	"	"	"	117.11	94.57	22.54	0.072 x 2.02 x 6.03	25.52	9.012	1.40
Average	bronze..........	Pb 0.2 (maximum)....			"	117.22	94.53	22.68	....	25.55	9.059	1.40
	BRONZES.											
C 79	Cast bronze......		"	"	"	317.00	306.54	11.46	0.19 x 1.96 x 5.96	26.05	4.488	0.70
C 80	" "	Cu 90..............	"	"	"	319.38	308.76	10.62	0.19 x 1.96 x 5.97	26.10	4.151	0.64
C 81	" "	Sn 10..............	"	"	"	318.00	307.00	11.00	0.19 x 1.96 x 5.97	26.10	4.300	0.67
Average	" "				"	318.13	307.43	11.03	....	26.08	4.313	0.67
C 55	Rolled bronze.....		"	"	"	85.08	68.70	16.38	0.05 x 2.01 x 6.02	25.00	6.685	1.04
C 56	" "	Cu 98.7............	"	"	"	87.04	71.39	15.65	0.05 x 2.01 x 6.02	25.00	6.387	0.99
C 57	" "	Sn 1.3............	"	"	"	86.83	71.65	15.18	0.05 x 2.01 x 6.01	24.96	6.205	0.96
Average	" "				"	86.16	70.58	15.77	....	24.99	6.426	0.99
C 58	Rolled phosphor	Cu 94.4............	"	"	"	90.18	81.90	8.28	0.05 x 2.01 x 6.02	25.00	3.379	0.52
C 59	bronze..........	Sn 5.5............	"	"	"	90.37	82.35	8.02	0.05 x 2.01 x 6.01	24.96	3.278	0.51
C 60	Rolled phosphor	P 0.1............	"	"	"	90.10	83.33	6.77	0.05 x 2.01 x 6.02	25.00	2.763	0.43
Average	bronze..........				"	90.22	82.53	7.69	....	24.99	3.140	0.49
C 49	Rolled zinc	Cu 85-90, Zn 4 max.	"	"	"	111.36	106.87	4.49	0.06 x 2.01 x 6.01	25.12	1.823	0.28
C 50	phosphor bronze..	Sn 6-11, Pb 0.2 max.	"	"	"	110.67	106.67	4.00	0.06 x 2.01 x 6.01	25.12	1.624	0.25
C 51	Rolled zinc	P 0.5 max.	"	"	"	111.02	106.88	4.14	0.06 x 2.01 x 6.01	25.12	1.681	0.26
Average	phosphor bronze..				"	111.02	106.81	4.21	....	25.12	1.709	0.26
C 73	Cast leaded zinc		"	"	"	341.28	330.70	10.58	0.21 x 1.96 x 5.98	26.77	4.013	0.62
C 74	bronze..........	Cu 86, Pb 0.5........	"	"	"	342.82	331.81	11.01	0.21 x 1.96 x 5.98	26.77	4.196	0.65
C 75	Cast leaded zinc	Sn 12, Zn 1.5........	"	"	"	346.33	335.21	11.12	0.21 x 1.96 x 5.98	26.77	4.238	0.66
Average	bronze..........				"	343.46	332.57	10.89	....	26.77	4.149	0.64
C 85	Cast leaded bronze	Cu 76..............	"	"	"	414.97	404.98	9.99	0.25 x 1.97 x 6.00	27.63	3.689	0.57
C 86	" " "	Sn 10..............	"	"	"	416.71	406.83	9.88	0.25 x 1.97 x 6.00	27.63	3.648	0.56
C 87	" " "	Pb 15..............	"	"	"	414.32	405.61	8.71	0.25 x 1.97 x 6.00	27.63	3.216	0.50
Average	" " "				"	415.33	405.81	9.53	....	27.63	3.518	0.55
C 82	Cast leaded bronze	Cu 88.1............	"	"	"	380.51	370.40	10.11	0.22 x 1.98 x 5.95	27.05	3.811	0.59
C 83	" " "	Sn 9.9............	"	"	"	381.01	370.72	10.29	0.22 x 1.98 x 5.95	27.05	3.881	0.60
C 84	" " "	Pb 2.0............	"	"	"	379.07	368.49	10.58	0.22 x 1.98 x 5.95	27.05	3.991	0.62
Average	" " "				"	380.20	369.87	10.33	....	27.05	3.894	0.60
	CUPRO-NICKEL.											
C 37	Rolled cupro-nicke		"	"	"	89.83	70.12	19.71	0.05 x 2.01 x 6.01	24.96	8.057	1.25
C 38	(coin metal)......	Cu 75..............	"	"	"	89.58	70.26	19.32	0.05 x 2.01 x 6.02	25.00	7.885	1.22
C 39	Rolled cupro-nicke	Ni 25..............	"	"	"	89.59	70.37	19.22	0.05 x 2.01 x 6.01	24.96	7.857	1.22
Average	(coin metal)......				"	89.67	70.25	19.42	....	24.97	7.933	1.23

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[a] The chemical compositions, as given, were submitted by the manufacturers and are in most instances only approximate type compositions.

[b] During the test there were two days when the test was discontinued and water drained from the boxes.

TABLE 6.—*Composition and loss in weight of test specimens exposed to action of Calumet mine water —Continued*

Test piece number.	Designation.	Approximate chemical composition[a], per cent.	Date.		Days immersed.	Weight, in grams.		Loss in weight, in grams.	Dimensions of test specimens, in inches.	Area of test specimens, in square inches.	Loss in milligrams, per sq. inch per day.	Loss in milligrams, per sq. cm. per day.
			Immersed.	Removed.		Before immersion.	After immersion.					
1	2	3	4	5	6	7	8	9	10	11	12	13
	CUPRO-NICKEL.											
C 31	Rolled cupro-nicke	Cu 85............... Ni 15...............	Dec. 20, 1921	Mar. 30, 1922	98[b]	84.30	64.31	19.90	0.047 x 2.01 x 6.01	24.91	8.187	1.27
C 32	" " "		"	"	"	85.69	65.77	19.92	0.047 x 2.01 x 6.03	25.00	8.148	1.26
C 33	" " "		"	"	"	85.65	66.36	19.29	0.047 x 2.01 x 6.03	25.00	7.873	1.22
					"	85.21	65.48	19.73	....	24.97	8.069	1.25
C 1	Cast leaded cupro-nickel............	Cu 50-60............ Ni 20-30............ Pb 20-30............	"	"	"	598.37	581.78	16.59	0.33 x 1.96 x 6.00	28.77	5.884	0.91
C 2			"	"	"	580.25	567.18	13.07	0.34 x 1.96 x 6.00	28.93	4.610	0.71
C 3	Cast leaded cupro-nickel............		"	"	"	600.51	586.16	13.35	0.34 x 1.96 x 6.00	28.93	4.709	0.73
Average					"	593.04	578.34	14.30	....	28.88	5.068	0.78
C 4	Cast chromium-iron cupro-nickel............	Cu 35-45, Fe 12-20... Ni 35-45 ... Ferro-Chromium 6-16	"	"	"	530.23	510.68	19.55	0.34 x 1.91 x 5.97	28.17	7.082	1.10
C 5			"	"	"	517.94	498.13	19.81	0.34 x 1.91 x 5.97	28.17	7.175	1.11
C 6			"	"	"	517.65	497.70	19.95	0.34 x 1.91 x 5.97	28.17	7.226	1.12
Average					"	521.97	498.87	19.77	....	28.17	7.161	1.11
C112	Cast iron manganese cupro-nickel............	Cu 75............... Ni 15............... Fe and Mn, balance....	"	"	"	219.44	196.68	22.76	0.13 x 1.99 x 6.01	26.00	8.932	1.38
C113			"	"	"	212.95	191.24	21.71	0.12 x 1.99 x 6.02	25.88	8.559	1.33
C114			"	"	"	207.22	185.42	21.80	0.12 x 2.00 x 6.01	25.96	8.568	1.33
Average					"	213.20	191.11	22.09	....	25.95	8.686	1.35
	NICKEL SILVER.											
C 13	Rolled iron nickel silver............	Cu 63.8............ Zn 17.7............ Ni 18.5............	"	"	"	87.38	67.47	19.91	0.05 x 2.00 x 6.04	24.96	8.139	1.26
C 14			"	"	"	87.59	68.07	19.52	0.05 x 2.00 x 6.04	24.96	7.980	1.24
C 15	Rolled iron nickel silver............		"	"	"	88.26	68.24	20.02	0.05 x 2.01 x 6.04	25.09	8.142	1.26
Average					"	87.74	67.93	19.82	....	25.00	8.087	1.25
C 43	Rolled nickel silver	Cu 60-70, Ni 9-15.... Zn 20-25, Fe 1- 4....	"	"	"	90.27	69.38	20.89	0.052 x 1.99 x 6.03	24.83	8.584	1.33
C 44	" " "		"	"	"	89.31	68.32	20.99	0.052 x 2.01 x 6.08	25.08	8.540	1.32
C 45	" " "		"	"	"	88.86	67.66	21.20	0.052 x 2.02 x 6.04	25.24	8.570	1.33
Average	" " "				"	89.48	68.45	21.03	....	25.05	8.565	1.33

C 34	Rolled nickel silver	Cu 52	"	"	"	82.54	57.49	25.05	0.05 x 2.00 x 6.00	24.80	10.306	1.60
C 35	" " "	Zn 36		"	"	83.13	58.46	24.67	0.05 x 2.00 x 6.00	24.80	10.150	1.57
C 36	" " "	Ni 12	"	"	"	84.58	59.23	25.35	0.05 x 2.00 x 6.00	24.80	10.429	1.61
Average	" " "				"	83.42	58.39	25.02	....	24.80	10.295	1.59
C 10	Cast silicon nickel		"	"	"	192.40	172.19	20.21	0.11 x 1.96 x 6.00	25.27	8.160	1.26
C 11	silver	Cu 49, Zn 25	"	"	"	200.76	181.16	19.60	0.12 x 1.97 x 6.00	25.55	7.827	1.21
C 12	Cast silicon nickel	Ni 25, Si 1	"	"	"	184.04	164.04	20.00	0.11 x 1.98 x 6.00	25.52	7.996	1.24
Average	silver				"	192.40	172.46	19.94	....	25.45	7.994	1.24
C 7	Cast tin-lead nickel	Cu 60, Zn 14	"	"	"	383.37	369.59	13.78	0.228 x 1.95 x 5.99	26.98	5.211	0.81
C 8	silver	Ni 15, Pb 8	"	"	"	384.49	371.72	12.77	0.228 x 1.95 x 5.99	26.98	4.829	0.75
C 9	Cast tin-lead nickel	Sn 3	"	"	"	383.97	371.42	12.55	0.229 x 1.95 x 5.99	27.00	4.742	0.74
Average	silver				"	383.94	370.91	13.03	....	26.99	4.927	0.76
	ALUMINUM ALLOYS.											
C 88	Cast Al-Si alloy		"	"	"	118.27	110.56	7.71	0.23 x 1.98 x 5.99	27.39	2.872	0.45
C 89	" " "	Al 95	"	"	"	117.62	110.29	7.33	0.23 x 1.98 x 5.99	27.39	2.780	0.42
C 90	" " "	Si 5	"	"	"	118.57	111.32	7.25	0.23 x 1.98 x 5.99	27.39	2.703	0.42
Average	" " "				"	118.15	110.72	7.43	....	27.39	2.768	0.43
C 91	Cast Al-Mn alloy		"	"	"	116.88	110.26	6.62	0.23 x 1.98 x 5.92	27.07	2.495	0.39
C 92	" " "	Al 98	"	"	"	116.81	110.13	6.68	0.23 x 1.98 x 5.92	27.07	2.517	0.39
C 93	" " "	Mn 2	"	"	"	115.83	109.10	6.73	0.23 x 1.98 x 5.92	27.07	2.536	0.39
Average	" " "				"	116.51	109.80	6.68	....	27.07	2.516	0.39
C 94	Rolled Al-Mn alloy		"	Feb. 2, 1922	42[b]	26.37	23.34	3.03	0.05 x 1.99 x 5.98	24.60	2.932	0.45
C 95	" " "	Composition not fur-	"	"	"	26.39	23.43	2.96	0.05 x 1.99 x 5.98	24.60	2.864	0.44
C 96	" " "	nished	"	"	"	26.24	23.27	2.97	0.05 x 1.99 x 5.98	24.60	2.874	0.45
Average	" " "				"	26.33	23.35	2.99	....	24.60	2.890	0.45
C 97	Rolled Al alloy		"	"	"	27.46	24.93	2.53	0.05 x 2.01 x 6.02	25.00	2.409	0.37
C 98	" " "	Composition not fur-	"	"	"	27.48	24.93	2.55	0.05 x 2.01 x 6.01	24.96	2.432	0.38
C 99	" " "	nished	"	"	"	27.30	24.73	2.57	0.05 x 2.01 x 6.02	25.00	2.447	0.38
Average	" " "				"	27.41	24.86	2.55	....	24.99	2.429	0.38
	HIGH SILICON CAST IRON.											
C130	High silicon cast	Si 13-14	"	Mar. 30, 1922	98[b]	274.32	235.30	39.02	0.21 x 1.99 x 5.94	26.97	14.762	2.29
C131	iron	Graphite, 1.3	"	"	"	366.85	326.19	40.66	0.28 x 1.98 x 5.92	27.86	14.891	2.31
C132	High silicon cast	Fe, balance	"	"	"	274.16	233.74	40.42	0.21 x 2.01 x 5.92	27.13	15.202	2.36
Average	iron				"	305.11	265.08	40.08	....	27.32	14.952	2.22
C133	High silicon cast	Si 14-14.5, P 0.16-0.20	"	"	"	390.81	390.75	0.06	0.29 x 2.02 x 5.98	28.80	0.0213	0.0083
C134	iron	C 0.2-0. 6, S .05 max.	"	"	"	389.30	389.27	0.03	0.29 x 2.05 x 6.00	29.27	0.0105	0.0016
C135	High silicon cast	Mn 0.35 (approximate)	"	"	"	393.68	393.65	0.03	0.29 x 2.05 x 6.00	29.27	0.0105	0.0016
Average	iron	Fe, balance			"	391.26	391.22	0.04	....	29.11	0.0141	0.0022

[a] *The chemical compositions, as given, were submitted by the manufacturers and are in most instances only approximate type compositions.*

[b] *During the test there were two days when the test was discontinued and water drained from the boxes.*

TABLE 6.—*Composition and loss in weight of test specimens exposed to action of Calumet mine water —Concluded.*

Test piece number.	Designation	Approximate chemical composition[a], per cent.	Date.		Days immersed.	Weight, in grams.		Loss in weight, in grams.	Dimensions of test specimens, in inches.	Area of test specimens, in square inches.	Loss in milligrams, per sq. inch per day.	Loss in milligrams, per sq. cm. per day.
			Immersed.	Removed.		Before immersion.	After immersion.					
1	2	3	4	5	6	7	8	9	10	11	12	13
	RUSTLESS STEEL.											
C106	Rolled high chromium rustless steel........	Cr 29.5, Mn 0.27.... C 0.36, Si 0.53.... Fe, balance..........	Dec. 20, 1921	Mar. 30, 1922	98[b]	94.79	94.79	0.00	0.07 x 2.01 x 6.02	25.32	0.0000	0.0000
C107			"	"	"	96.19	96.18	0.01	0.06 x 2.01 x 6.00	25.08	0.0041	0.0006
C108			"	"	"	96.32	96.31	0.01	0.07 x 2.01 x 6.01	25.28	0.0040	0.0006
Average					"	95.77	95.76	0.01	....	25.23	0.0027	0.0004
C100	Rolled rustless steel "A".........	Highly alloyed Cr-Ni-Si steel........	"	"	"	97.14	96.82	0.32	0.065 x 2.01 x 5.99	25.12	0.1299	0.0201
C101			"	"	"	98.43	97.63	0.80	0.065 x 2.00 x 6.01	25.08	0.3254	0.0504
C102	Rolled rustless steel "A"........		"	"	"	97.78	96.89	0.89	0.065 x 2.00 x 6.02	25.12	0.3615	0.0560
Average					"	97.78	97.11	0.67	....	25.11	0.2723	0.0422
C103	Rolled rustless steel "B"........	Highly alloyed Cr-Ni-Si steel........	"	"	"	107.05	106.34	0.71	0.07 x 2.06 x 6.00	25.87	0.2800	0.0434
C104			"	"	"	104.17	103.39	0.78	0.07 x 2.00 x 6.03	25.24	0.3153	0.0488
C105	Rolled rustless steel "B"...... .		"	"	"	106.05	105.47	0.58	0.07 x 2.02 x 6.05	25.57	0.2314	0.0358
Average					"	105.76	105.07	0.69	....	25.56	0.2756	0.0427
	MISCELLANEOUS METALS AND ALLOYS.											
	METALS.											
C115	Rolled pure ingot iron.............	Fe 99.9.............	"	Feb. 16, 1922	56[b]	78.03	60.44	17.59	0.05 x 2.01 x 5.99	24.88	12.625	1.96
C116			"	"	"	80.36	59.59	20.77	0.05 x 2.01 x 6.09	25.17	14.735	2.28
C117	Rolled pure ingot iron.............		"	"	"	80.51	61.18	19.33	0.05 x 2.01 x 6.11	25.87	13.605	2.11
Average					"	79.63	60.40	19.23	....	25.14	13.655	2.12
C109	Rolled pure aluminum.......	Pure aluminum.......	"	Feb. 2, 1922	42[b]	26.64	23.83	2.81	0.05 x 1.99 x 6.01	24.72	2.706	0.42
C110			"	"	"	26.59	23.81	2.78	0.05 x 1.99 x 6.00	24.68	2.681	0.42
C111	Rolled pure aluminum.........		"	"	"	26.98	24.17	2.81	0.05 x 1.99 x 6.00	24.68	2.710	0.42
Average					"	26.74	23.94	2.80	....	24.69	2.699	0.42

C 25	Rolled pure copper		"	Mar. 30, 1922	98[b]	94.47	74.01	20.46	0.053 x 2.02 x 6.00	25.09	8.321	1.29
C 26	" " "	Pure copper.........	"	"	"	94.73	73.56	21.17	0.053 x 2.03 x 6.00	25.21	8.568	1.33
C 27	" " "		"	"	"	94.79	74.27	20.52	0.053 x 2.02 x 6.00	25.09	8.345	1.29
Average	" " "				"	94.66	73.95	20.72	....	25.13	8.411	1.30
C121	Rolled nickel......		"	"	"	89.47	70.67	18.80	0.05 x 2.00 x 6.04	24.96	7.685	1.19
C122	" "	Ni 99...............	"	"	"	88.94	70.47	18.47	0.05 x 2.00 x 6.03	24.92	7.562	1.17
C123	" "		"	"	"	89.23	70.47	18.76	0.05 x 2.00 x 6.04	24.96	7.669	1.19
Average	" "				"	89.21	70.54	18.68	....	24.95	7.639	1.18
	ALLOYS.											
C 76	Cast aluminum		"	"	"	252.74	246.70	6.04	0.19 x 1.90 x 5.87	25.25	2.440	0.38
C 77	bronze..........	Cu 90...............	"	"	"	254.87	248.13	6.74	0.19 x 1.90 x 5.87	25.25	2.723	0.42
C 78	Cast aluminum	Al 10...............	"	"	"	253.82	247.06	6.76	0.19 x 1.90 x 5.87	25.25	2.727	0.42
Average	bronze..........				"	253.81	247.30	6.51	....	25.25	2.630	0.41
C 52	Rolled iron	Cu 85...............	"	"	"	97.62	78.04	19.58	0.06 x 1.99 x 5.98	24.76	8.069	1.25
C 53	aluminum bronze..	Fe 8...............	"	"	"	98.31	79.28	19.03	0.07 x 2.00 x 5.99	25.08	7.742	1.20
C 54	Rolled iron	Al 7...............	"	"	"	97.58	77.92	19.66	0.07 x 2.00 x 5.99	25.08	7.998	1.24
Average	aluminum bronze..				"	97.84	78.41	19.42	....	24.97	7.936	1.23
C 70	Cast Cu-Pb alloy..		"	"	"	413.16	401.16	12.00	0.226 x 1.90 x 6.00	26.37	4.643	0.72
C 71	" " "	Cu 50...............	"	"	"	410.17	397.79	12.38	0.224 x 1.91 x 6.00	26.46	4.774	0.74
C 72	" " "	Pb 50...............	"	"	"	400.06	388.43	11.63	0.22 x 1.91 x 6.00	26.40	4.495	0.70
Average	" " "				"	407.80	395.80	12.00	....	26.41	4.687	0.72
C 40	Rolled monel metal	Ni 67.0, Cu 28 ..	"	"	"	111.23	107.74	3.49	0.062 x 2.04 x 6.08	25.82	1.379	0.21
C 41	" " "	Mn 1.75, Fe 1.76..	"	"	"	109.49	90.32	19.17	0.062 x 2.04 x 6.09	25.86	7.564	1.17
C 42	" " "	C 0.2, Si 0.18..	"	"	"	112.01	92.77	19.24	0.064 x 2.04 x 6.07	25.81	7.606	1.18
Average	" " "	S 0.026 ..			"	110.91	96.94	13.97	....	25.83	5.516	0.86
C 61	Rolled Cu-Mn-Fe	Cu 95...............	"	"	"	88.31	67.87	20.44	0.05 x 2.01 x 6.02	25.00	8.342	1.29
C 62	alloy............	Mn 4...............	"	"	"	86.27	65.71	20.56	0.05 x 2.01 x 6.02	25.00	8.391	1.30
C 63	Rolled Cu-Mn-Fe	Fe 1...............	"	"	"	86.69	65.86	20.83	0.05 x 2.01 x 6.02	25.00	8.502	1.32
Average	alloy............				"	87.09	66.48	20.61	....	25.00	8.412	1.30
C118	Rolled nichrome...	Ni 58-62, Cr 12-14...	"	"	"	78.78	77.91	0.87	0.05 x 1.99 x 6.05	24.88	0.357	0.06
C119	" " ...	Fe 25 Si 0.5 ...	"	"	"	79.20	78.23	0.97	0.05 x 2.00 x 6.03	24.92	0.397	0.06
C120	" " ...	Mn 1.25-1.50 ...	"	"	"	78.80	77.92	0.88	0.05 x 1.99 x 6.05	24.88	0.361	0.06
Average	" " ...				"	78.93	78.02	0.91	....	24.89	0.372	0.06

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[a] *The chemical compositions, as given, were submitted by the manufacturers and are in most instances only approximate type compositions.*

[b] *During the test there were two days when the test was discontinued and water drained from the boxes.*

TABLE 7.—*Composition and average loss in weight of test specimens exposed to action of mine water from Montour No. 1, Edna No. 2, and Calumet mines.*

Designation.	Approximate chemical composition[a], per cent.	Montour mine No 1. Average free acidity[b], 1430 ppm.; average total acidity[c], 11,360 ppm.		Edna mine No. 2. Average free acidity[b], 2160 ppm.; average total acidity[c], 14,160 ppm.		Calumet mine. Average free acidity[b], 430 ppm.; average total acidity[c], 2950 ppm.	
		Test specimen numbers, "A" series.	Average loss in milligrams per sq. cm., per day.	Test specimen numbers, "B" series.	Average loss in milligrams per sq. cm., per day.	Test specimen numbers, "C" series.	Average loss in milligrams per sq. cm., per day.
BRASSES.							
Rolled high brass	Cu 66.6, Zn 33.4	16, 17, 18	1.87	16, 17, 18	7.27	16, 17, 18	1.42
Rolled low brass	Cu 80, Zn 20	19, 20, 21	2.31	19, 20, 21	7.15	19, 20, 21	1.39
Rolled Naval brass	Cu, 60.4, Zn 38.8, Sn 0.8	22, 23, 24	1.28	22, 23, 24	7.11	22, 23, 24	1.39
Rolled brass (Admiralty metal), grain size 0.025 mm.	Cu 70, Zn 29, Sn 1	28, 29, 30	1.69	28, 29, 30	7.07	28, 29, 30	1.10
Rolled brass (Admiralty metal), grain size 0.035 mm.	Cu 70, Zn 29, Sn 1	64, 65, 66	1.64	64, 65, 66	6.45	64, 65, 66	0.90
Rolled brass (Admiralty metal), grain size 0.075 mm.	Cu 70, Zn 29, Sn 1	67, 68, 69	1.69	67, 68, 69	6.47	67, 68, 69	0.79
Rolled manganese bronze	Cu 57-60, Sn 0.5-1.5, Zn 37-40, Fe 0.8-2, Mn 0.3 (max.), Pb 0.2 (max.)	46, 47, 48	1.48	46, 47, 48	6.68	46, 47, 48	1.40
BRONZES.							
Cast bronze	Cu 90, Sn 10	79, 80, 81	0.66	79, 80, 81	2.12	79, 80, 81	0.67
Rolled bronze	Cu 98.7, Sn 1.3	55, 56, 57	1.74	55, 56, 57	6.68	55, 56, 57	1.00
Rolled phosphor bronze	Cu 94.4, Sn 5.5, P 0.1	58, 59, 60	0.83	58, 59, 60	4.68	58, 59, 60	0.49
Rolled zinc phosphor bronze	Cu 85-90, Sn 6-11, P 0.5 (max.), Zn 4, Pb 0.2 (max.)	49, 50, 51	0.89	49, 50, 51	1.70	49, 50, 51	0.27
Cast leaded zinc bronze	Cu 86, Sn 12, Pb 0.5, Zn 1.5	73, 74, 75	0.15	73, 74, 75	0.83	73, 74, 75	0.64
Cast leaded bronze	Cu 75, Pb 15, Sn 10	85, 86, 87	0.66	85, 86, 87	1.26	85, 86, 87	0.55
Cast leaded bronze	Cu 88.1, Sn 9.9, Pb 2	82, 83, 84	0.60	82, 83, 84	2.56	82, 83, 84	0.60
CUPRO-NICKEL.							
Rolled cupro-nickel (coin metal)	Cu 75, Ni 25	37, 38, 39	1.56	37, 38, 39	7.34	37, 38, 38	1.23
Rolled cupro-nickel	Cu 85, Ni 15	31, 32, 33	1.67	31, 32, 33	7.47	31, 32, 33	1.25
Cast leaded cupro-nickel	Cu 50-60, Ni 20-30, Pb 20-30	1, 2, 3	1.16	1, 2, 3	4.07	1, 2, 3	0.79
Cast chromium-iron cupro-nickel	Cu 35-45, Fe 12-20, Ni 35-45, Ferro-Chromium 6-16	4, 5, 6	1.44	4, 5, 6	6.68	4, 5, 6	1.11
Cast, iron manganese cupro-nickel	Cu 75, Ni 15, Fe and Mn balance	112, 113, 114	1.99	112, 113, 114	6.82	112, 113, 114	1.35

NICKEL SILVER.							
Rolled nickel silver	Cu 63.8, Zn 17.7, Ni 18.5	13, 14, 15	1.63	13, 14, 15	7.07	13, 14, 15	1.25
Rolled iron nickel silver	Cu 60-70, Zn 20-25, Ni 9-15, Fe 1-4	43, 44, 45	1.69	43, 44, 45	7.45	43, 44, 45	1.33
Rolled nickel silver	Cu 52, Zn 36, Ni 12	34, 35, 36	1.73	34, 35, 36	7.24	34, 35, 36	1.60
Cast silicon nickel silver	Cu 49, Zn 25, Ni 25, Si 1	10, 11, 12	1.73	10, 11, 12	7.04	10, 11, 12	1.24
Cast tin-lead nickel silver	Cu 60, Ni 15, Zn 14, Pb 8, Sn 3	7, 8, 9	1.08	7, 8, 9	4.22	7, 8, 9	0.76
Cast tin-lead nickel silver	Cu 57, Ni 19.5, Zn 16, Pb 6, Sn 2	136, 137, 138	0.87	136, 137, 138	4.47	....	....
ALUMINUM ALLOYS.							
Cast Al-Si alloy	Al 95, Si 5	88, 89, 90	2.25	88, 89, 90	2.20	88, 89, 90	0.43
Cast Al-Mn alloy	Al 98, Mn 2	91, 92, 93	0.84	91, 92, 93	2.23	91, 92, 93	0.39
Rolled Al-Mn alloy	Composition not furnished	94, 95, 96	1.59	94, 95, 96	2.03	94, 95, 96	0.45
Rolled Al alloy	Composition not furnished	97, 98, 99	0.59	97, 98, 99	1.77	97, 98, 99	0.38
HIGH SILICON CAST IRON.							
High silicon cast iron	Si 13-14, graphite 1.3, Fe balance	130, 131, 132	2.72	130, 131, 132	4.89	130, 131, 132	2.22
High silicon cast iron	Si 14-14.5, P 0.16-0.20, C 0.2-0.6, S 0.5 (max.), Mn 0.35 (approx.). Fe, balance	133, 134, 135	0.00037	133, 134, 135	0.00374	133, 134, 135	0.0022
RUSTLESS STEEL.							
Rolled high chromium steel	Cr 29.5, Mn 0.27, C 0.36, Si 0.53, Fe, balance	106, 107, 108	0.00031	106, 107, 108	0.00030	106, 107, 108	0.0004
Rolled rustless steel "A"	Highly alloyed Cr-Ni-Si steel	100, 101, 102	0.00051	100, 101, 102	0.00015	100, 101, 102	0.0422
Rolled rustless steel "B"	Highly alloyed Cr-Ni-Si steel	103, 104, 105	0.045	103, 104, 105	0.00074	103, 104, 105	0.0427
MISCELLANEOUS METALS AND ALLOYS.							
METALS.							
Rolled pure ingot iron	Fe 99.9	115, 116, 117	3.45	115, 116, 117	7.14	115, 116, 117	2.12
Rolled pure aluminum	Pure aluminum	109, 110, 111	0.84	109, 110, 111	1.55	109, 110, 111	0.42
Rolled pure copper	Pure copper	25, 26, 27	1.89	25, 26, 27	7.06	25, 26, 27	1.30
Rolled nickel	Ni 99	121, 122, 123	1.46	122, 123	0.00299	121, 122, 123	1.18
ALLOYS.							
Cast aluminum bronze	Cu 90, Al 10	76, 77, 78	0.90	76, 77, 78	5.09	76, 77, 78	0.41
Rolled iron aluminum bronze	Cu 85, Fe 8, Al 7	52, 53, 54	1.50	52, 53, 54	6.02	52, 53, 54	1.23
Cast Cu-Pb alloy	Cu 50, Pb 50	70, 71, 72	0.48	70, 71, 72	3.87	70, 71, 72	0.72
Rolled monel metal	Ni 67.0, Cu 28, Mn 1.75, Fe 1.76, C 0.2, Si 0.18, S 0.026	40, 41, 42	1.36	40, 41, 42	6.72	40, 41, 42	0.86
Rolled Cu-Mn-Fe alloy	Cu 95, Mn 4, Fe 1	61, 62, 63	1.86	61, 62, 63	7.38	61, 62, 63	1.30
Rolled Ni-Cr-Fe alloy	Ni 65, Cr 16, Mn 0.7, Si 0.7, Al 0.15, Fe, balance	....	....	139, 140, 141	7.45	....	....
Rolled nichrome	Ni 58-62, Cr 12-14, Fe 25, Mn 1.25-1.50, Si 0.5	118, 119, 120	0.02451	118, 119, 120	0.01812	118, 119, 120	0.058

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[a] *The chemical compositions, as given, were submitted by the manufacturers and are in most instances only approximate type compositions.*

[b] *Free acidity is expressed in parts per million in terms of sulphuric acid and is the acidity due to free sulphuric acid.*

[c] *Total acidity is expressed in parts per million in terms of sulphuric acid and is the acidity due to free sulphuric acid plus sulphates of iron and aluminum*

TABLE 8.—*General appearance of test pieces at completion of corrosion tests.*

Test piece number.	Designation.	Approximate chemical composition[a], per cent.	Montour No. 1 mine.	Edna No. 2 mine.	Calumet mine.
1	2	3	4	5	6
	BRASSES.				
16, 17, 18	Rolled high brass	Cu 66.6 Zn 33.4	Coating easily removable[b]. Uniform corrosion.	Coating easily removable. Considerable uniform corrosion.	Coating easily removable. Uniform corrosion.
19, 20, 21	Rolled low brass	Cu 80 Zn 20	Coating easily removable. Nodules of copper crystals adhere to pieces. See text under "Phenomena observed."	Coating easily removable. Considerable uniform corrosion.	Coating easily removable. Uniform corrosion.
22, 23, 24	Rolled Naval brass	Cu 60.4 Zn 38.8 Sn 0.8	Coating easily removable. Slight uniform corrosion, surface cracks develop on bending.	Coating removable with difficulty. Pieces brittle and easily broken.	Coating removable with difficulty. Uniform corrosion.
28, 29, 30	Rolled brass (Admiralty metal), grain size 0.025 mm.	Cu 70 Zn 29 Sn 1	Coating easily removable. Uniform corrosion.	Coating easily removable Considerable uniform corrosion.	Coating easily removable. Uniform corrosion.
64, 65, 66	Rolled brass (Admiralty metal), grain size 0.035 mm.	Cu 70 Zn 29 Sn 1	Coating easily removable. Considerable corrosion, elongated, shallow pits.	Coating easily removable. Considerable corrosion, elongated, shallow pits.	Coating easily removable. Corrosion with elongated, shallow pits.
67, 68, 69	Rolled brass (Admiralty metal), grain size 0.075 mm.	Cu 70 Zn 29 Sn 1	Coating easily removable. Considerable corrosion, elongated, shallow pits.	Coating easily removable. Considerable corrosion, elongated, shallow pits.	Coating easily removable. Corrosion with elongated, shallow pits.
46, 47, 48	Rolled manganese bronze	Cu 57-60 Zn 37-40 Fe 0.8-2 Sn 0.5-1.5 Mn 0.3 (max.) Pb 0.2 (max.)	No coating, very slight uniform corrosion. Surface cracks develop on bending.	Coating easily removable. Considerable uniform action. Pieces brittle.	Coating easily removable. Uniform corrosion.
	BRONZES.				
79, 80, 81	Cast bronze	Cu 90 Sn 10	Coating partially removable. Slight uniform corrosion.	Coating partly removable. Irregular corrosion[c].	Coating not removable. Uniform corrosion.
55, 56, 57	Rolled bronze	Cu 98.7 Sn 1.3	Coating easily removable. Irregular corrosion.	Coating easily removable. Considerable irregular corrosion.	Coating easily removable. Irregular corrosion.

58, 59, 60	Rolled phosphor bronze	Cu 94.4 Sn 5.5 P 0.1	Coating easily removable. Irregular corrosion.	Coating easily removable. Considerable irregular corrosion.	Coating easily removable. Irregular corrosion.
49, 50, 51	Rolled zinc phosphor bronze	Cu 85-90 Sn 6-11 Zn 4 (max.) Pb 0.2 (max.) P 0.5 (max.)	Coating removable with difficulty. Irregular corrosion.	Coating removable with difficulty. Uniform corrosion.	Coating easily removable. Slight uniform corrosion.
73, 74, 75	Cast leaded zinc bronze	Cu 86 Sn 12 Zn 1.5 Pb 0.5	Coating not removable. Very slight uniform corrosion.	Coating not removable. Uniform corrosion.	Coating not removable. Uniform corrosion.
85, 86, 87	Cast leaded bronze	Cu 75 Sn 10 Pb 15	Coating partly removable. Slight uniform corrosion.	Coating partly removable. Irregular corrosion.	Coating not removable. Uniform corrosion.
82, 83, 84	Cast leaded bronze	Cu 88.1 Sn 9.9 Pb 2	Coating partly removable. Slight uniform corrosion.	Coating removable with difficulty. Irregular corrosion.	Coating not removable. Uniform corrosion.
	CUPRO-NICKEL.				
37, 38, 39	Rolled cupro-nickel (coin metal)	Cu 75 Ni 25	Coating easily removable. Uniform corrosion.	Coating easily removable. Considerable uniform corrosion.	Coating easily removable. Uniform corrosion.
31, 32, 33	Rolled cupro-nickel	Cu 85 Ni 15	Coating easily removable. Uniform corrosion.	Coating easily removable. Considerable uniform corrosion.	Coating easily removable. Uniform corrosion.
1, 2, 3	Cast leaded cupro-nickel	Cu 50-60 Ni 20-30 Pb 20-30	Coating removable with difficulty. Uniform corrosion.	Coating removable with difficulty. Uniform corrosion.	Coating removable with difficulty. Uniform corrosion.
4, 5, 6	Cast chromium-iron cupro-nickel	Cu 35-45 Fe 12-20 Ni 35-45 Ferro-Chromium 6-16	Coating easily removable. Uniform corrosion.	Coating removable with difficulty. Local pitting. Uniform corrosion.	Coating removable with difficulty. Uniform corrosion.
112, 113, 114	Cast, iron manganese cupro-nickel	Cu 75 Ni 15 Fe and Mn, balance	Coating easily removable. Uniform corrosion.	Coating easily removable. Considerable uniform corrosion.	No coating. Uniform corrosion.
	NICKEL SILVER.				
13, 14, 15	Rolled nickel silver	Cu 63.8 Ni 18.5 Zn 17.7	Coating easily removable. Uniform corrosion.	Coating easily removable. Considerable uniform corrosion.	Coating easily removable. Uniform corrosion.
43, 44, 45	Rolled iron nickel silver	Cu 60-70 Zn 20-25 Ni 9-15 Fe 1- 4	Coating easily removable. Uniform corrosion.	Coating easily removable. Considerable uniform corrosion.	Coating easily removable. Uniform corrosion.

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[a] The chemical compositions, as given, were submitted by the manufacturers and are in most cases only approximate type compositions.

[b] "Coating removable with difficulty," i. e., can be removed by rubbing with fiber brush in water.
"Coating not removable," i. e., cannot be removed by rubbing with fiber brush in water.
"Coating easily removable," i. e., can be removed by rubbing with hands in water.
"No coating," i. e., no coating visible to naked eye.

[c] Irregular corrosion, i. e., patches or nodules of metal remain above the corroded surface.

TABLE 8.—*General appearance of test pieces at completion of corrosion tests—Continued.*

Test piece number.	Designation.	Approximate chemical composition[a], per cent.	Montour No. 1 mine.	Edna No. 2 mine.	Calumet mine.
1	2	3	4	5	6
	NICKEL SILVER.				
34, 35, 36	Rolled nickel silver	Cu 52 Zn 36 Ni 12	Coating easily removable. Uniform corrosion.	Coating easily removable. Considerable uniform corrosion.	Coating easily removable. Uniform corrosion.
10, 11, 12	Cast silicon nickel silver	Cu 49 Ni 25 Zn 25 Si 1	Coating easily removable. Uniform corrosion, slight uniform pitting (pits very small).	Coating easily removable. Considerable uniform corrosion.	Coating removable with difficulty. Uniform corrosion.
7, 8, 9	Cast tin-lead nickel silver	Cu 60 Ni 15 Zn 14 Pb 8 Sn 3	Coating removable with difficulty. Uniform corrosion, slight local pitting.	Coating removable with difficulty. Uniform corrosion, slight local pitting.	Coating removable with difficulty. Uniform corrosion.
136, 137, 138	Cast tin-lead nickel silver	Cu 57 Ni 19.5 Zn 16 Pb 6 Sn 2	Coating removable with difficulty. Uniform corrosion.	Coating removable with difficulty. Uniform corrosion.	
	ALUMINUM ALLOYS.				
88, 89, 90	Cast Al-Si alloy	Al 95 Si 5	Coating removable with difficulty. Irregular pitting (pits large).	Coating removable with difficulty. Irregular pitting (pits large).	No coating. Irregular pitting (pits large).
91, 92, 93	Cast Al-Mn alloy	Al 98 Mn 2	No coating. Irregular pitting (pits large).	No coating. Irregular pitting (pits large).	No coating. Irregular pitting (pits large).
94, 95, 96	Rolled Al-Mn alloy	Composition not furnished	No coating. Corrosion with irregular pitting, pin holes through metal.	No coating. Irregular pitting, pin holes through metal.	No coating. Irregular pitting, pin holes through metal.
97, 98, 99	Rolled Al alloy	Composition not furnished	No coating. Corrosion with irregular pitting, pin holes through metal.	No coating. Corrosion with irregular pitting pin holes through metal.	No coating. Irregular pitting, pin holes through metal.
	HIGH SILICON CAST IRON.				
130, 131, 132	High silicon cast iron	Si 13-14 Graphite 1.3 Fe, balance	Coating partly removable. Uniform corrosion.	Coating partly removable. Uniform corrosion.	Coating partly removable. Uniform corrosion.

133, 134, 135	High silicon cast iron..........	Si 14-14.5 .... P 0.16-0.20 .... C 0.2-0.6 .... S 0.05 (max.) .... Mn 0.35 (approx.).... Fe, balance	No coating. No visible corrosion.	No coaitng. No visible corrosion.	Coating removable with difficulty. No visible corrosion.
	RUSTLESS STEEL.				
106, 107, 108	Rolled high chromium rustless steel......................	Cr 29.5 .... Mn 0.27............ C 0.36............ Si 0.53............ Fe, balance..........	No coating. No visible corrosion.	No coating. No visible corrosion.	Coating removable with difficulty. No visible action.
100, 101, 102	Rolled rustless steel "A"........	Highly alloyed Cr-Ni-Si steel......	No coating. No visible corrosion.	No coating. No visible corrosion.	Coating not removable. Slight uniform action.
103, 104, 105	Rolled rustless steel "B".......	Highly alloyed Cr-Ni-Si steel......	No coating. No visible corrosion.	No coating. No visible corrosion.	Coating not removable. Slight uniform action.
	MISCELLANEOUS METALS AND ALLOYS.				
	METALS.				
115, 116, 117	Rolled pure ingot iron..........	Fe 99.9.............	Coating removable with difficulty. Considerable uniform corrosion and pin holes through metal.	Coating removable with difficulty. Considerable uniform corrosion and pin holes through metal.	Coating partly removable. Uniform corrosion and pin holes through metal.
109, 110, 111	Rolled pure aluminum..........	Pure aluminum.......	No coating. Considerable corrosion with irregular pitting. Pits are shallow and elongated.	Coating easily removable. Corrosion, with irregular pitting. Pits shallow and elongated. Pin holes through metal.	No coating. Corrosion, with irregular pitting and pin holes through metal.
25, 26, 27	Rolled pure copper.............	Pure copper.........	Coating easily removable. Uniform corrosion.	Coating easily removable. Considerable uniform corrosion.	No coating. Uniform corrosion.
121, 122, 123	Rolled nickel.................	Ni 99...............	Coating not removable. Slight uniform corrosion.	Coating not removable. No visible corrosion.	Coating not removable. Uniform corrosion.
	ALLOYS.				
76, 77, 78	Cast aluminum bronze.........	Cu 90............... Al 10...............	Coating removable with difficulty. Slight uniform corrosion.	Coating removable with difficulty. Irregular corrosion.	Coating not removable. Uniform corrosion.

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[a] The chemical compositions, as given, were submitted by the manufacturers and are in most cases only approximate type compositions.

[b] "Coating removable with difficulty," i. e., can be removed by rubbing with fiber brush in water.
"Coating not removable," i. e., cannot be removed by rubbing with fiber brush in water.
"Coating easily removable," i. e., can be removed by rubbing with hands in water.
"No coating," i. e., no coating visible to naked eye.

[c] Irregular corrosion, i. e., patches or nodules of metal remain above the corroded surface.

TABLE 8.—*General appearance of test pieces at completion of corrosion tests—Concluded.*

Test Piece Number.	Designation.	Approximate chemical composition[a], per cent.	Montour No. 1 mine.	Edna No. 2 mine.	Calumet mine.
1	2	3	4	5	6
	ALLOYS.				
52, 53, 54	Rolled iron aluminum bronze	Cu 85 Fe 8 Al 7	Coating easily removable. Irregular corrosion.	Coating easily removable. Considerable uniform corrosion.	Coating easily removable. Uniform corrosion.
70, 71, 72	Cast Cu-Pb alloy	Cu 50 Pb 50	Coating easily removable. Slight irregular corrosion.	Coating easily removable. Uniform corrosion with some irregular pitting.	Coating easily removable. Irregular corrosion.
40, 41, 42	Rolled monel metal	Ni 67.0 Cu 28 Mn 1.75 Fe 1.76 C 0.2 Si 0.18 S 0.026	Coating easily removable. Uniform corrosion.	Coating easily removable. Considerable uniform corrosion.	Coating easily removable. Uniform corrosion.
61, 62, 63	Rolled Cu-Mn-Fe alloy	Cu 95 Mn 4 Fe 1	Coating easily removable. Irregular corrosion.	Coating easily removable. Considerable uniform corrosion.	Coating easily removable. Uniform corrosion.
139, 140, 141	Rolled Ni-Cr-Fe alloy	Ni 65 Cr 16 Mn 0.7 Si 0.7 Al 0.15 Fe, balance		Coating easily removable. Irregular corrosion and pitting.	
118, 119, 120	Rolled nichrome	Ni 58 -62 Fe 25 Cr 12 -14 Mn 1.25- 1.50 Si 0.5	No coating. No visible corrosion.	No coating. No visible corrosion.	Coating partly removable. Slight uniform corrosion.

[a] The chemical compositions, as given, were submitted by the manufacturers and are in most cases only approximate type compositions.

[b] "Coating removable with difficulty," i. e., can be removed by rubbing with fiber brush in water.
"Coating not removable," i. e., cannot be removed by rubbing with fiber brush in water.
"Coating easily removable," i. e., can be removed by rubbing with hands in water.
"No coating," i. e., no coating visible to naked eye.

[c] Irregular corrosion, i. e., patches or nodules of metal remain above the corroded surface.

TABLE 9.—*Physical properties*[a] *(submitted by manufacturers) of metals and alloys.*

Test piece number.	Designation.	Approximate composition. (Submitted by manufacturers)	Physical properties.
1	2	3	4
	BRASSES.		
16, 17, 18	Rolled high brass	Cu 66.6 Zn 33.4	Sp. gr., 8.48. Melting point, 1630° F., approximate. Hardness, 60 (Brinell), approximate. Tensile strength, 50,000 lb. per sq. in. Electrical resistivity, 39 ohms per cir. mil-foot. Average coefficient of expansion (25-300°), 0.0000201. Grain size, 0.030 mm., approximate. Cold worked. Annealed at about 500° C. This metal can be drawn. It cannot be machined easily. It cannot be forged or drop-forged. Values given are for light annealed metal.
19, 20, 21	Rolled low brass	Cu 80 Zn 20	Sp. gr., 8.67. Melting point, 1700° F., approximate. Hardness, 60 (Brinell), approximate. Tensile strength, 45,000 lbs. per sq. in., approximate. Electrical resistivity, 32 ohms per cir. mil-foot, approximate. Average coefficient of expansion (25-300° C.), 0.0000191. Grain size, 0.020 mm., approximate. Cold worked. Annealed at about 500° C. This metal can be drawn. It cannot be machined easily. It cannot be forged or drop-forged. Values given are for light annealed metal.
22, 23, 24	Rolled Naval brass	Cu 60.4 Zn 38.8 Sn 0.8	Sp. gr., 8.4, approximate. Melting point, 1560° F., approximate. Hardness, 80 (Brinell), approximate. Tensile strength, 50,000-60,000 lbs. per sq. in. Electrical resistivity, 42 ohms per cir. mil-foot, approximate. Average coefficient of expansion (25-300° C.), 0.0000214. Hot and cold worked. Annealed at about 560° C. This metal can be drawn, forged, drop-forged and machined.
28, 29, 30	Rolled brass (Admiralty metal-, grain size 0.025 mm.	Cu 70 Zn 29 Sn 1	Hardness, 17.5 Scleroscope; Erichsen, 12.39 mm. Tensile strength, 57,450 lbs. per sq. in. Grain size, 0.025 mm. Cold worked. Annealed one-half hour at 400° C. This metal can be drawn, welded, machined, It cannot be forged or drop-forged.
64, 65, 66	Rolled brass (Admiralty metal-, grain size 0.035 mm.	Cu 70 Zn 29 Sn 1	Sp. gr., 8.5. Tensile strength, 60,000 lbs. per sq. in. Grain size, 0.035 mm. Cold worked. This metal can be drawn, welded, forged and machined. It cannot be drop-forged.
67, 68, 69	Rolled brass (Admiralty metal-, grain size 0.075 mm.	Cu 70 Zn 29 Sn 1	Sp. gr., 8.5. Tensile strength, 50,000 lbs. per sq. in. Grain size, 0.075 mm. Cold worked. This metal can be drawn, welded, forged and machined. It cannot be drop-forged.
46, 47, 48	Rolled manganese bronze	Cu 57-60 Zn 37-40 Fe 0.8-2.0 Sn 0.5-1.5 Mn 0.3 (max.) Pb 0.2 (max.)	Sp. gr., 8.414. Melting point, 1480° F. Hardness, 140-165 (Brinell). Tensile strength, 65,000 to 70,000 lbs. per sq. in. Hot and cold worked and annealed. This metal can be drawn, forged, drop-forged and machined.
	BRONZES.		
79, 80, 81	Cast bronze	Cu 90 Sn 10	Sp. gr., 8.6. Hardness, 61-70 (Brinell). Tensile strength, 30,000-36,000 lbs. per sq. in. Compression strength, 0.1 in. at 45,000 lbs. Contraction allowance in casting, 3/16 in. This metal can be welded and machined. It cannot be rolled, drawn or forged.

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[a] *All the data, regarding physical properties, given in this table were submitted by the manufacturers.*

TABLE 9.—*Physical properties*[a] *(submitted by manufacturers) of metals and alloys—Continued.*

Test piece number.	Designation.	Approximate composition. (Submitted by manufacturers)	Physical properties.
1	2	3	4
55, 56, 57	Rolled bronze	Cu 98.7 Sn 1.3	Sp. gr., 8.97 at 20° C. Tensile strength, 42,000 lbs. per sq. in. (annealed). Electrical resistivity, 25.7 ohms per mil-foot. Coefficient of expansion, 0.0000169 per °C. Hot and cold worked. Annealed at 650° C. for 15 minutes. This metal can be drawn, welded, forged, drop-forged. It can be machined with difficulty.
58, 59, 60	Rolled phosphor bronze	Cu 94.4 Sn 5.5 P 0.1	Tensile strength, 50,000 lbs. per sq. in. (annealed). Cold worked. This metal can be drawn, welded, forged. It can be machined with difficulty.
49, 50, 51	Rolled zinc phosphor bronze	Cu 85-90 Sn 6-11 Zn 4 (max.) Pb 0.2 (max.) P 0.5 (max.)	Sp. gr., 8.9, approximate. Hardness, 37 (Shore), approximate. Cold worked and annealed. This metal can be drawn and machined.
73, 74, 75	Cast leaded zinc bronze	Cu 86 Sn 12 Zn 1.5 Pb 0.5	Sp. gr., 8.6. Hardness, 74-83 (Brinell). Tensile strength, 32,000-38,000 lbs. per sq. in. Compression strength, 0.27 in. at 100,000 lbs. Contraction allowance in casting, 3/16 in. This metal can be welded and machined. It cannot be drawn, rolled, forged or drop-forged.
85, 86, 87	Cast leaded bronze	Cu 75 Pb 15 Sn 10	Sp. gr., wt. per cu. in., 0.3175 lb. Melting point, approximate, 350° F. Tensile strength, 30,000 lbs. per sq. in. Compression strength, 22,000 lbs. Contraction allowance in casting, ¼ in. per ft. This metal can be machined. It cannot be rolled, drawn, welded, forged or drop-forged.
82, 83, 84	Cast leaded bronze	Cu 88.1 Pb 2 Sn 9.9	Sp. gr., 8.6. Melting point, 1780 °F. Hardness, 61 (Brinell, 10 mm. ball, 500 Kg. pressure). Tensile strength, 27,500 lbs. per sq. in. Transverse strength, 2713 lbs. per sq. in. Electrical resistivity, 93 ohms per mil-foot. Contraction allowance in casting, 3/16 in. per foot.
	CUPRO-NICKEL.		
37, 38, 39	Rolled cupro-nickel (coin metal)	Cu 75 Ni 25	Hardness, Scleroscope, Univ., 23.5; Erichsen, 8.60 mm. Tensile strength, 68,550 lbs. per sq. in. Cold worked and annealed 1 hour at 700° C. This metal can be drawn, welded, forged, drop-forged and machined.
31, 32, 33	Rolled cupro-nickel	Cu 85 Ni 15	Hardness, Scleroscope, Univ., 12.5; Erichsen, 10.73 mm. Tensile strength, 50,950 lbs. per sq. in. Grain size, 0.01 mm. Cold worked and annealed 1 hour at 650° C. This metal can be drawn, welded, forged, drop-forged and machined.
1, 2, 3	Cast leaded cupro-nickel	Cu 50-60 Pb 20-30 Ni 20-30	Sp. gr., 550 lbs. per cu. ft. Melting point, 2970° C. Hardness, 8, Scleroscope. Tensile strength, 30,000 lbs. per sq. in. Contraction allowance in casting, ¼ in to the foot. This metal can be machined. It cannot be rolled, drawn, welded, forged or drop-forged.

4, 5, 6	Cast chromium-iron cupro-nickel	Cu 35-45 Fe 12-20 Ni 35-45 Ferro-Chromium 6-16	Sp. gr., 536 lbs. per cu. ft. Melting point, 2975° F. Hardness, 21, Scleroscope. Tensile strength, 90,000 lbs. per sq. in. Electrical resistivity, 326 ohms per cir. mil-foot. Contraction allowance in casting, ¼ in. to the foot. This metal can be machined. It cannot be rolled, drawn, welded, forged or drop-forged.
112, 113, 114	Cast, iron manganese cupro-nickel	Cu 75 Ni 15 Fe and Mn, balance	Sp. gr., 8.58. Melting point, 2140° F., approximate. Hardness, 93 (Brinell with 500 Kg. load). Tensile strength, 67,000 lbs. per sq. in. Contraction allowance in casting ¼ in. per ft. This material can be machined. It can probably be rolled and drawn.
	NICKEL SILVER.		
13, 14, 15	Rolled nickel silver	Cu 63.8 Ni 18.5 Zn 17.7	Sp. gr., 8.75. Melting point about 2030° F. Hardness, 75 (Brinell), approximate. Tensile strength, 60,000 lbs. per sq. in., approximate. Electrical resistivity about 185 ohms per cir. mil-foot. This metal can be drawn. It cannot be forged or drop-forged. It cannot be machined easily, grain size about 0.020 mm. Cold worked. Annealed at about 700° C. Values given are for light annealed metal.
43, 44, 45	Rolled iron nickel silver	Cu 60-70 Zn 20-25 Ni 9-15 Fe 1-4	Sp. gr., 543 lbs. per cu. ft. Melting point, 2510° F. Hardness varies according to mechanical working. Tensile strength varies from 35,000 to 165,000 lbs. per sq. in., according to temperature. Electrical resistivity at 20° C., 6.55 per cent (International Standard). Coefficient of expansion, 0.000001645 per degree C. Cold worked. Annealed at 1400-1700° F. This metal can be rolled, drawn, welded, forged, drop-forged and machined.
34, 35, 36	Rolled nickel silver	Cu 52 Zn 36 Ni 12	Hardness, Scleroscope, Univ., 20.3; Erichsen, 12.15 mm. Tensile strength, 70,850 lbs. per sq. in. Grain size, 0.015 mm. Cold worked and annealed 1 hour at 550° C. This metal can be drawn, welded, forged, drop-forged and machined.
10, 11, 12	Cast silicon nickel silver	Cu 49 Ni 25 Zn 25 Si 1	Sp. gr., 8.84. Melting point, 2400° F. Hardness, 25-30 (Shore). Tensile strength, 70,000 lbs. per sq. in. Compression strength, 12,000-25,000 lbs. per sq. in. Contraction allowance in casting, ¼ in. per foot. This metal can be machined and welded. It cannot be rolled, drawn or drop-forged.
7, 8, 9	Cast tin-lead nickel silver	Cu 60 Ni 15 Zn 14 Pb 8 Sn 3	Sp. gr., 8.74. Hardness, 15-16, Scleroscope. Tensile strength, 30,000 lbs. per sq. in. Contraction allowance in casting, 0.185 in. per foot. This metal can be machined. It cannot be rolled, drawn, welded, forged or drop-forged.
136, 137, 138	Cast tin-lead-nickel silver	Cu 57 Ni 19.5 Zn 16 Pb 6 Sn 2	Sp. gr., 8.92. Melting point, 2100° F. Hardness, 59 (Brinell, 500 Kg. pressure). Tensile strength, 27,250 lbs. per sq. in.
	ALUMINUM ALLOYS.		
88, 89, 90	Cast Al-Si alloy	Al 95 Si 5	Sp. gr., 2.67. Melting point, 1140° F. Hardness, 38 (Brinell). Tensile strength, 16,000 lbs. per sq. in. Coefficient of expansion, 0.000023 in. per °C. Contraction allowance in casting, 5/32 in. per ft. This metal can be welded and machined. It cannot be rolled, drawn, forged or drop-forged.
91, 92, 93	Cast Al-Mn alloy	Al 98 Mn 2	Sp. gr., 2.75. Melting point, 1200° F. Hardness, 36 (Brinell). Tensile strength, 17,500 lbs. per sq. in. Coefficient of expansion, 0.000023 in. per °C. Contraction allowance in casting, 5/32 in. per ft. This metal can be rolled, drawn, welded, forged, drop-forged and machined.

All the data, regarding physical properties, given in this table were submitted by the manufacturers.

TABLE 9.—*Physical properties*[a] *(submitted by manufacturers) of metals and alloys—Concluded.*

Test piece number.	Designation.	Approximate composition. (Submitted by manufacturers)	Physical properties.
1	2	3	4
94, 95, 96	Rolled Al-Mn alloy	Composition not furnished	
97, 98, 99	Rolled Al alloy	Composition not furnished	
	HIGH SILICON CAST IRON.		
130, 131, 132	High silicon cast iron	Si 13-14 Graphite 1.3 Fe, balance	**Sp. gr., 7.0. Melting point, 2400-2500° F. Hardness, 260 (Brinell).** Contraction **allowance in casting, 3/16 in. This material can be machined on grinding.** It cannot be rolled, drawn, welded, forged or drop-forged.
133, 134, 135	High silicon cast iron	Si 14-14.5 P 0.16-0.20 C 0.2 -0.6 S 0.05 (max.) Mn 0.35 (approx.) Fe, balance	Sp. gr., 7.00. Melting point, 2300° F. Hardness, 49-51 (Shore). Tensile strength, 10,000 lbs. per sq. in., approximate. Transverse strength, 1,000 lbs., with deflection ⅛ in. Compression strength, 70,000 lbs. Electrical resistivity, 63.3 microhms per cu.cm., at 0° C.; 71.2 microhms per cu.cm., at 180° C.; 94.4 microhms per cu.cm., at 100° C. Coefficient of expansion, 0.00001565 per °F. Contraction allowance in casting, 3/16 in. per ft. Small close grains. This metal can be machined by grinding, can be welded with oxy-acetylene flame. It cannot be rolled, drawn, forged or drop-forged.
	RUSTLESS STEEL.		
106, 107, 108	Rolled high chromium rustless steel	Cr 29.5 Mn 0.27 C 0.36 Si 0.53 Fe, balance	Sp. gr., 7.8 approximate. Melting point varies from 2100-2732° F., depending on composition. Tensile strength varies from 60,000 to 120,000 lbs. per sq. in., depending on composition and treatment. Transverse strength, 7000-10,000 lbs. Electrical resistivity, 80 microhms per cu. cm., at 1000° C. Hot rolled and annealed. This metal can be drawn, welded, forged, drop-forged and machined.
100, 101, 102	Rolled rustless steel "A"	Highly alloyed Cr-Ni-Si steel	Sp. gr., 7.76. Melting point, 2700° F., estimated. Hardness, 30 to 65, Scleroscope (depending on whether hot rolled, cold rolled or annealed). Tensile strength, 65,000-150,000 lbs. per sq. in. ultimate (depending on whether hot rolled, cold rolled or annealed). Coefficient of expansion at 20-300° C., 0.0000159; at 600-900° C., 0.0000179. Samples submitted were hot rolled and annealed. This metal can be rolled to 0.008 in. in sheet, welded by acetylene, forged at 1900° F., drop-forged at 1900-2000° F.; machined, when annealed.
103, 104, 105	Rolled rustless steel "B"	Highly alloyed Cr-Ni-Si steel	Sp. gr., 7.76. Melting point, 2700° F., estimated. Hardness, 30 to 65, Scleroscope (depending on whether hot rolled, cold rolled or annealed). Tensile strength, 65,000-150,000 lbs. per sq. in. ultimate (depending on whether hot rolled, cold rolled or annealed). Coefficient of expansion at 20-300° C., 0.0000159; at 600-900° C., 0.0000179. Samples submitted were hot rolled and annealed. This metal can be rolled to 0.008 in. in sheet, welded by acetylene, forged at 1900° F., drop-forged at 1900-2000° F.; machined, when annealed.

	MISCELLANEOUS METALS AND ALLOYS. METALS.		
115, 116, 117	Rolled pure ingot iron	Fe 99.9	Melting point, 2795° F. Hardness, 95-120 (Brinell). Tensile strength, 40,000 lbs. per sq. in. Transverse strength, 30,000 lbs. per sq. in. Compression strength, 40,000 lbs. per sq. in. Electrical resistivity, 10.7 microhms per cu.cm. Coefficient of expansion per °C., 0.000011 (0-100° C.). Cold rolled. This metal can be drawn, welded, forged, drop-forged and machined.
109, 110, 111	Rolled pure aluminum	Pure aluminum	
25, 26, 27	Rolled pure copper	Pure copper	
121, 122, 123	Rolled nickel	Ni 99	Sp. gr., 8.99. Melting point, 2646° F. Hardness, 139-150 (Brinell). Tensile strength, 70,000-110,000 lbs. per sq. in. Coefficient of expansion, 0.000129 per °C. Cold worked. Annealed at 1650° F. This metal can be drawn, welded, forged, drop-forged and machined.
	ALLOYS.		
76, 77, 78	Cast aluminum bronze	Cu 90 Al 10	Sp. gr., 7.5. Hardness, 80-100 (Brinell). Tensile strength, 65,000-70,000 lbs. per sq. in. Compression strength, 0.1 in. at 80,000 lbs. Contraction allowance in casting, 0.22 in. This metal can be rolled, drawn, welded, forged, drop-forged and machined.
52, 53, 54	Rolled iron aluminum bronze	Cu 85 Fe 8 Al 7	Sp. gr., 7.63. Melting point, 1800° F. Hardness controlled from 20-48 (Scleroscope). Tensile strength, 65,000-90,000 lbs. per sq. in. Coefficient of expansion same as steel. Can be either hot or cold worked. Cannot be annealed. This metal can be drawn, welded, forged, drop-forged and machined.
70, 71, 72	Cast Pb-Cu alloy	Cu 50 Pb 50	
40, 41, 42	Rolled monel metal	Ni 67.0 Cu 28 Mn 1.75 Fe 1.76 C 0.2 Si 0.18 S 0.026	Sp. gr., 8.94. Melting point, 2480° F. Hardness, 162 (Brinell). Tensile strength, 80,000-105,000 lbs. per sq. in. Compression strength, 67,000 lbs. per sq. in. Electrical resistivity, 256 ohms per mil-foot. Thermal conductivity, 1/15 that of copper. Coefficient of expansion, 0.0000134 per °C. (22.5-100° C.). Hot rolled. This metal can be drawn, forged, drop-forged and machined. It can be autogeneous welded, but not hammer welded.
61, 62, 63	Rolled Cu-Mn-Fe alloy	Cu 95 Mn 4 Fe 1	Hardness, 77 (Brinell). Tensile strength, 50,000 lbs. per sq. in. (annealed). Hot and cold worked. This metal can be drawn, welded, forged and drop-forged. It can be machined with difficulty.
139, 140, 141	Rolled Ni-Cr-Fe alloy	Ni 65 Cr 16 Mn 0.7 Si 0.7 Al 0.15 Fe, balance	Melting point, 2670° F. Hardness, 40 (Shore). Hot rolled.
118, 119, 120	Rolled nichrome	Ni 58-62 Fe 25 Cr 12-14 Mn 1.25-1.50 Si 0.5	Sp. gr., 8.29. Melting point, 2660° F., approximate. Hardness, 27-30 (Shore). Tensile strength, 102,200 lbs. per sq. in. Coefficient of expansion, +0.0000116 per °C. (at 0-100° C.). Cold worked. Annealed at 1800° F. This metal can be drawn, welded, forged, drop-forged and machined.

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[a] *All the data, regarding physical properties, given in this table were submitted by the manufacturers.*

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Bulletin 5

COAL-MINING INVESTIGATIONS

UNDER AUSPICES OF

CARNEGIE INSTITUTE OF TECHNOLOGY,
UNITED STATES BUREAU OF MINES, AND
ADVISORY BOARD OF COAL-MINE OPERATORS
AND ENGINEERS.

MICROSTRUCTURAL ASPECTS OF METALS AND ALLOYS CORRODED BY ACID MINE WATER

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PREFACE.

Pittsburgh is the greatest industrial center in America, and the heart of the greatest bituminous coal-mining district in the world. It is eminently desirable, therefore, that this city should have an institution which devotes a part of its great facilities to the scientific study of that branch of the industry which is largely responsible for Pittsburgh's development and that of Western Pennsylvania.

On May 27, 1919, a number of leading representatives of the coal-mining industry of Western Pennsylvania met in conference with the then President of the Carnegie Institute of Technology with a view of bringing about closer relations between the Institute and the mining interests. It was felt that the advice and co-operation of men in the field were necessary for the training of young men for mining work, and at the conclusion of the meeting the following resolution was adopted:

> That this gathering give its approval and moral and material support to the form of education proposed for the Carnegie Institute of Technology by which students may receive a combined technical, practical, and business training, necessary to fit them for service in the coal mining and allied industries. Further, that the President of the Carnegie Institute of Technology appoint a board of no less than ten men representing the coal mining and allied industries, the United States Bureau of Mines, the State Department of Mines, and the Carnegie Institute of Technology, who will advise and assist in carrying out this program of education and training, particularly in its practical phases to the mining industry and in its cooperation with the United States Bureau of Mines.

Following further the intention of this resolution, the President of the Institute entered into a co-operative agreement on June 1, 1919, with the Director of the United States Bureau of Mines whereby full advantage could be taken of the Bureau's laboratories, equipment, and library, as well as of the advice and instruction of its technical staff.

To carry out this new program there was organized during the summer months the Co-operative Mining Courses in the Department of Mining and Metallurgical Engineering, College of Engineering, of the Institute. The course in mining engineering covers four years, and leads to the degree of Bachelor of Science. The two-year course in coal mining is planned to prepare men with a certain amount of practical experience for executive positions. The four-weeks intensive summer course in coal mining is designed for miners who aspire to be firebosses and mine foremen. In a large measure, the new mining, ore-dressing, and coal-washing laboratories at the Institute have been equipped gratuitously by various manufacturers of mining machinery and appliances. Co-operative research through teaching and research fellowships is devoted to various problems in coal mining and the utilization of fuels. The Institute selects the fellows, the Bureau of Mines provides the laboratory facilities, and the Advisory Board determines what problems be undertaken, and publishes the reports.

The primary object of this co-operation of the Carnegie Institute of Technology, the United States Bureau of Mines, and the Advisory Board of Coal Mine Operators and Engineers is the proper education and training of young men for the mining industry. The ultimate objective is to bring about better conditions and greater efficiency in mining operations. The decrease in reserves of coal and increasing cost of production make it urgently necessary for mine operators and engineers to take advantage of everything which modern science, machinery, and methods can contribute.

EDWARD STEIDLE,
Supervisor, Cooperative Mining Courses,
Carnegie Institute of Technology.

FOREWORD.

The investigation described in this paper was conducted by the Co-operative Mining Courses of the Department of Mining of the Carnegie Institute of Technology and the Pittsburgh Experiment Station of the U. S. Bureau of Mines, in co-operation with the coal-mining industry of western Pennsylvania. Under co-operative agreement, four research fellowships paying $750 per school year of 10 months are supported by the Carnegie Institute. These fellowships are open to properly qualified graduates of universities and technical schools. The research work is carried on in the laboratories of the Bureau of Mines under the direction of a member of the Bureau research staff, and results are published under the joint authorship of the two investigators.

Fellowship holders are required to register at the Institute as graduate students and become candidates for the degree of Master of Science, unless an equivalent degree has been previously earned. The purpose of these fellowships is the solution of problems in mining and utilization of coal.

This bulletin is a supplement to Bulletin 4, "Corrosion Tests on Metals and Alloys in Acid Mine Waters from Coal Mines".

The corroded test specimens of metals and alloys which had been immersed in the acid mine waters; together with uncorroded samples of the same materials, were subjected to microscopic examination and study with a view to obtaining information on the mechanism of corrosion in relation to the microstructure of the materials.

It was found that (1) in brasses the grain size had little if any effect upon the rate or nature of the corrosion; (2) there was selective corrosion in some of the brasses and bronzes; (3) some of the alloys, especially bronzes, after being cleaned free from adhering coating, or precipitate, retained a very hard coating which seems to be protective to a large degree; (4) no protective coating could be detected on the corrosion resisting high-silicon iron, high-chromium steel, chromium-nickel-silicon steels, and nichrome.

Results of additional corrosion tests of 10 alloys in flowing mine water are given in an appendix to Bulletin 5. These tests are supplementary to those described in Bulletin 4.

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Acknowledgment is gratefully made to A. C. Fieldner, superintendent and supervising chemist of the Pittsburgh Experiment Station of the Bureau of Mines, under whose general supervision the work was carried out; to W. A. Selvig for co-operation in the mine-water tests; to Edward Steidle, supervisor, Co-operative Mining Courses at Carnegie Institute of Technology; and to Charles H. Eldridge and George B. Dalrymple, who made the chemical analyses of the metals and alloys.

Acknowledgment is also made to the following companies who kindly co-operated by supplying test specimens of metals and alloys:

Ackermite Company of America, The
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Aluminum Company of America
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American Brass Co., The
American Manganese Bronze Co., The
American Metal Products Co.
American Rolling Mill Co., The
Aterite Company, The
Bethlehem Foundry and Machine Co.
Bridgeport Brass Co.
Bronze Die Casting Co.
Cleveland Brass Manufacturing Co., The
Crane Company of Chicago
Crucible Steel Company of America
Driver-Harris Company
Duriron Company, Inc., The
Hendricks Brothers, Inc.
Ingersoll-Rand Company
International Nickel Co., The
Lumen Bearing Co.
Midwest Engine Co.
Rich Tool Co.
Scovill Manufacturing Co.
Union Carbide and Carbon Research Laboratories, Inc.
United Lead Co., The
Waukesha Foundry Co.
William Cramp Sons Ship & Engine Building Co., The

MICROSTRUCTURAL ASPECTS OF METALS AND ALLOYS CORRODED BY ACID MINE WATER.

By ROBERT J. ANDERSON *and* GEORGE M. ENOS.

INTRODUCTION.

During the course of a previous investigation[1] on the corrosion of metals and alloys in acid mine water, a number of phenomena were observed in the behavior of the materials tested, particularly in connection with their rates of corrosion, the formation of coatings on the surfaces, and the relation of chemical composition to corrosion rates and coating formation. The tests reported in Bulletin 4 were carried out simply for the purpose of determining the corrodibility of various metals and alloys in acid mine water, and the data so obtained were expected to be of use in the selection of alloys for employment in mining equipment. Inasmuch as these tests were solely empirical, their application in the study of the mechanism of corrosion was necessarily limited; and since it was not possible to determine from the data why one metal or alloy corroded more rapidly than another, the work was extended to include microsopic study of the corroded metals and alloys. It was thought that microscopic examination of the various samples corroded in the previous investigation might throw light on the causes for corrosion under the particular condition involved, and that data obtained from such study might also be of value in studying the fundamentals of corrosion. Accordingly, examination was made under the microscope of the many samples of metals and alloys which had been corroded in acid mine water during the investigation reported in Bulletin 4. Study was made of the metals and alloys in their original condition and after corrosion. The actual microscopic work was carried out by the junior author in the Metallurgical Laboratory of the Non-Ferrous Metals Section of the Bureau of Mines, under the direction of the senior author.

Table 1 gives the designation, test-piece numbers, and the chemical composition of the metals and alloys included in the previous investigation, and also similar data on a few metals and alloys corroded since the conclusion of the investigation reported in Bulletin 4. Data and discussion of the behavior in mine water of these last mentioned alloys will be found on pages 36 to 42 of this Bulletin (No. 5). The data in Table 1 have been taken from Table 7 of Bulletin 4, with the following exception: The chemical compositions have been revised to give exact compositions, rather than the nominal compositions given in Bulletin 4; the analyses, with the exception of those noted in the table, were made in the laboratory of the Non-Ferrous Metals Section of the Bureau of Mines.

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[1] Selvig, W. A., and Enos, George M., Corrosion tests on metals and alloys in acid mine waters from coal mines: Bull. 4, Carnegie Institute of Technology, 1922, 71 pp.

TABLE 1.—*Designation, chemical composition, and numbers of test pieces.*

Designation.	Chemical composition, per cent.	Test piece numbers.
	Brasses.	
Rolled high brass	[a]Cu, 66.55; Zn, 33.45	16, 17, 18
Rolled low brass	[a]Cu, 80.09; Zn, 19.91	19, 20, 21
Rolled Naval brass	[a]Cu, 60.40; Sn, 0.77; Zn, 38.83	22, 23, 24
Rolled brass (Admiralty metal) grain size 0.025 mm	Cu, 70.80; Sn, 1.14; Zn, 28.06	28, 29, 30
Rolled brass (Admiralty metal) grain size 0.035 mm	Cu, 71.38; Zn, 27.36; Sn, 1.26	64, 65, 66
Rolled brass (Admiralty metal) grain size 0.075 mm	Cu, 71.46; Zn, 27.42; Sn, 1.12	67, 68, 69
Rolled brass	Cu, 57.95; Pb, trace; Sn, 0.47; Fe, 0.55; Zn, 41.02	46, 47, 48
	Manganese Brasses.	
Cast manganese brass	Cu, 68.05; Zn, 27.89; Fe, 1.55, Pb, 0.45; Mn, 2.06	142, 143, 144
Cast manganese brass	Cu, 67.45; Zn, 28.84; Fe, 1.48; Pb, 0.28; Mn, 1.95	145, 146, 147
Rolled manganese brass	Cu, 67.10; Zn, 29.64; Fe, 0.97; Pb, 0.30; Mn, 1.99	148, 149, 150
Rolled manganese brass	Cu, 65.5; Pb, 0.5; Zn, 30.5, Mn, 2.2; Fe, 1.3	151, 152, 153
	Bronzes.	
Cast bronze	Cu, 89.8; Sn, 9.7; Pb, 0.5	79, 80, 81
Rolled bronze	Cu, 98.51; Sn, 1.49	55, 56, 57
Rolled phosphor bronze	[a]Cu, 94.4; Sn, 5.5; P, 0.1	58, 59, 60
Rolled leaded phosphor bronze	Cu, 89.8; Sn, 5.6; Pb, 4.6; Fe, trace; P, trace	49, 50, 51
Cast leaded-zinc bronze	Cu, 86.34; Pb, 0.83; Sn, 11.24; Zn, 1.60	73, 74, 75
Cast leaded bronze	Cu, 74.9; Pb, 14.3; Sn, 10.5	85, 86, 87
Cast leaded bronze	Cu, 87.5; Sn, 10.6; Pb, 1.6	82, 83, 84
	Cupro-nickels.	
Rolled cupro-nickel (coin metal)	Cu, 74.60; Ni, 25.40	37, 38, 39
Rolled cupro-nickel	Cu, 84.36; Ni, 15.64	31, 32, 33
Cast leaded cupro-nickel	Cu, 53.57; Ni, 25.30; Fe, 0.61; Pb, 19.58; Sn, 0.56	1, 2, 3
Cast chromium-iron cupro-nickel	Cu, 42.24; Cr, 11.89; Ni, 35.00; Si, 1.50; Fe, 9.35	4, 5, 6
Cast iron manganese cupro-nickel	Cu, 71.16; Fe, 7.47; Ni, 19.01; Mn, 2.35	112, 113, 114

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[a] Analyses furnished by co-operating company.

TABLE 1.—*Designation, chemical composition, and numbers of test pieces.* —Continued.

Designation.	Chemical composition, per cent.	Test piece numbers.
	Nickel silvers.	
Rolled nickel silver	[a]Cu, 63.78; Zn, 17.68; Ni, 18.54	13, 14, 15
Rolled iron-nickel silver	Cu, 66.03; Zn, 23.99; Ni, 9.92; Fe, 0.05	43, 44, 45
Rolled nickel silver	Cu, 52.79; Zn, 34.58; Ni, 12.63	34, 35, 36
Cast silicon-nickel silver	Cu, 72.3; Ni, 16.5; Sn, 3.5; Zn, 7.4; Pb, 0.3; Si, trace	10, 11, 12
Cast tin-lead nickel silver	Cu, 63.52; Ni, 12.85; Sn, 4.59; Zn, 11.55; Pb, 7.49	7, 8, 9
Cast tin-lead nickel silver	Cu, 54.32; Sn, 2.54; Zn, 16.33; Pb, 6.30; Ni, 20.51	136, 137, 138
	Copper-lead alloys.	
Cast copper-lead alloy	Cu, 53.4; Pb, 46.4	70, 71, 72
Cast copper-lead alloy	Cu, 68.0; Pb, 31.9	157, 158, 159
Cast copper-lead alloy	Cu, 73.01; Pb, 26.96	160, 161, 162
	Aluminum alloys.	
Cast aluminum-silicon alloy	Si, 3.90; Al (by difference), 96.1	88, 89, 90
Cast aluminum-manganese alloy	Mn, 1.81; Al (by difference), 98.19	91, 92, 93
Rolled aluminum-manganese alloy	Mn, 0.95; Fe, 0.95; Si, 0.53; Al (by difference), 97.57	94, 95, 96
Rolled aluminum alloy	Cu, 3.62; Mn, 0.46; Fe, 0.45; Si, 0.56; Al (by difference), 94.91	97, 98, 99
	High-silicon cast irons.	
High-silicon cast iron	Si, 14.50; C, 1.45	130, 131, 132
High-silicon cast iron	Si, 13.80; C, 0.76	133, 134, 135
	Rustless steels.	
Rolled high-chromium steel	Cr, 29.5; Mn, 0.27; Si, 0.53; C, low; Fe, remainder	106, 107, 108
Rolled alloy steel	Ni, 23.87; Cr, 12.96; Si, 3.40; C, low; Fe, remainder	100, 101, 102
Rolled alloy steel	Ni, 29.60; Si, 3.26; Cr, 10.73; C, low; Fe, remainder	103, 104, 105
	Miscellaneous metals and alloys.	
	Metals.	
Rolled ingot iron	[a]Fe, 99.9	115, 116, 117
Rolled aluminum	[a]Commercially pure aluminum	109, 110, 111
Rolled copper	[a]Commercially pure copper	25, 26, 27
Rolled nickel	[a]Ni, 99+	121, 122, 123
	Alloys.	
Cast aluminum bronze	Cu, 93.9; Al, 6.1	76, 77, 78
Rolled iron-aluminum bronze	Cu, 86.23; Fe, 4.81; Al (by difference), 8.96	52, 53, 54
Rolled monel metal	Ni, 65.1; Cu, 30.52; Fe, 4.2	40, 41, 42
Cast high-lead alloy	Pb, 96.1; alkaline earth metals, remainder	154, 155, 156
Rolled copper-manganese-iron alloy	Cu, 94.81; Mn, 4.52; Fe, 0.67	61, 62, 63
Rolled nickel-chromium-iron alloy	Ni, 52.50; Al, 0.20; Cr, 9.29; Si, 0.19; Mn, 1.24; Fe, remainder	139, 140, 141
Rolled nichrome	Ni, 57.44; Si, 0.55; Cr, 9.37; Mn, 1.75; Fe, remainder	118, 119, 120

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[a] Analyses furnished by co-operating company.

PREVIOUS WORK ON THE MICROSCOPY OF CORRODED METALS AND ALLOYS.

Not much work dealing with the microscopy of corrosion has been reported in the literature. The principal investigations may be of interest, however, and these are cited below:

Desch[2] and his collaborators have studied the micro-chemistry of the corrosion of some non-ferrous alloys after exposure to salt-water solutions. They conclude (1) that in the brasses, de-zincification takes place—that is, zinc is removed and copper left *in situ;* (2) that the total corrosion of the alpha alloys of copper and zinc is less than that of the beta alloys; (3) that in alpha brass the initial stage of corrosion is but little affected by annealing; (4) in alpha-and-beta brass the unannealed alloy is de-zincified more than the annealed alloy, and the total corrosion is more; (5) in the annealed alpha-and-beta brass, corrosion first proceeds through the beta areas and then spreads to the alpha areas; (6) de-zincification is the cause of pitting; and (7) there is no essential difference between electrolytically accelerated and natural corrosion in sea water. In the zinc-bronze groups they find that the total corrosion is less than that of the bronzes under similar conditions.

In another paper, Desch[3] discusses the effect of the physical condition of the metal on the rate of corrosion. He states that local cold working greatly accelerates corrosion. He also notes the protective effect of certain metals such as lead, tin, and manganese, particularly in alpha-and-beta brass. The various papers by Desch and his collaborators were illustrated by appropriate photomicrographs.

In the Fourth, Fifth and Sixth Reports to the Corrosion Committee of the Institute of Metals, Bengough[4] and his associates in connection with their study of the corrosion of condenser tubes in sea water, investigated the initial stages of corrosion. It will be recalled that Desch and his co-workers submit that the corrosion of condenser tubes is due in most cases to de-zincification, but from their microscopic study and other observations on the corrosion of condenser tubes, Bengough and others question the views of Desch, and state that de-zincification in most cases, is apparent, rather than real, and that the true explanation of the coppery layer usually found on corroded condenser tubes is to be found in considering the copper as being re-deposited from solution. This view is also held by Abrams[5], who has shown that the presence of a membrane—which may be of almost any material—or of copper salts in excess, will cause re-deposition of copper after previous solution of both the copper and zinc. Study has also been made of the microscopy of the corrosion of condenser tubes by Lasche[6] and by v. Wurstemberger[7].

---

[2] Desch, C. H., and Whyte, S., The micro-chemistry of corrosion: Part I—Some copper-zinc alloys: *Jour.* Inst. of Metals, vol. 10, 1913, pp. 304-323.

Whyte, S., and Desch, C. H., The micro-chemistry of corrosion: Part II—The alpha-alloys of copper and zinc: *Jour.* Inst. of Metals, vol. 11, 1914, pp. 235-245.

Whyte, S., The micro-chemistry of corrosion: Part III—The alpha-beta alloys of copper and zinc: *Jour.* Inst. of Metals, vol. 13, 1915, pp. 80-90.

Desch, C. H., and Hyman, H., The micro-chemistry of corrosion: Part IV—Gun-metal: *Jour.* Inst. of Metals, vol. 14, 1915, pp. 189-197.

[3] Desch, C. H., Physical and mechanical factors in corrosion: Trans. Faraday Soc., vol. 11, March, 1916, pp. 198-203.

[4] Bengough, G. D., and Hudson, O. F., Fourth Report to the Corrosion Committee of the Institute of Metals: *Jour.* Inst. of Metals, vol. 21, 1919, pp. 37-214.

Bengough, G. D., Jones, R. M., and Pirret, R., Fifth Report to the Corrosion Committee of the Institute of Metals: *Jour.* Inst. of Metals, vol. 23, 1920, pp. 65-135.

Bengough, G. D., and Stuart, J. M., Sixth Report to the Corrosion Research Committee of the Institute of Metals: The nature of corrosive action, and the function of colloids in corrosion, with an appendix in terms used in colloid chemistry, *Jour.* Inst. of Metals, vol. 28, 1922, pp. 31-114.

Rawdon and Merica have also made contributions to the literature of the microscopy of corrosion. The former[8] found that in corrosion in sea water both the alpha and the beta constituents are attacked. A definite zone in which the beta phase only is attacked separates the unchanged metal from the completely corroded portion.

In a paper on metallic coatings for rust prevention, Rawdon[9] and his associates have also made use of the microscope to observe the changes which had taken place when the metals were corroded.

Corrosion is frequently associated with stress in the embrittling of metals. Rawdon[10] and his associates have investigated this subject and the results are embodied in two recent papers.

The structure of the corroded coating on tinned sheet copper has been studied by Merica[11].

---

[5] Abrams, R. B., The de-zincification of brass: Paper presented at the 42nd general meeting of the Am. Electrochem. Soc., Montreal, Sept., 1922.

[6] Lasche, O., Anfressungen an Kondensatorrœhren: *Zeit. f. Metallkunde*, vol. 12 (pp. 161-178) (1920).

[7] Wurstemberger, von, F., Selektive Korrosionen und Entzinkunserscheinungen an Messingteilen: *Zeit. f. Metallkunde*, vol. 14, 1922, pp. 23-59.

[8] Rawdon, H. S., Typical cases of the deterioration of Muntz metal (60:40) brass by selective corrosion: Bureau of Standards Tech. Paper 103, 1917, 28 pp.

[9] Rawdon, H. S., Grossman, M. A., and Finn, A. N., Metallic coatings for rust-proofing iron and steel: Part II—*Chem. and Met. Eng.*, vol. 20, 1919, pp. 530-537.

[10] Rawdon, H. S., Kryntsky, A. I., and Berliner, J. F. T., Brittleness developed in aluminum and duralumin by stress and corrosion: *Chem. and Met. Eng.*, vol. 26, 1922, pp. 154-158.

Rawdon, H. S., Kryntsky, A. I., and Berliner, J. F. T., Brittleness developed in pure lead by stress and corrosion: *Chem. and Met. Eng.*, vol. 26, 1922, pp. 109-111.

[11] Merica, P. D., Structure of the coating on tinned sheet copper in relation to a specific case of corrosion: Bureau of Standards Tech. Paper 90, 1917, 17 pp.

Giolitti and Ceccarelli[12] found that the presence of the alpha and beta constituents hastens corrosion, and that non-homogenous alpha bronze also corrodes in bronzes containing from 0 to 10 per cent tin.

The study of the failure of brass because of "season cracking" or corrosion cracking is a subject which has received much attention lately. Undoubtedly the kind and rate of corrosion is affected by the stresses present in any metal. Merica and his associates have discussed the failure of brass in a series of technical papers,[13] and two groups of discussions[14] by technical societies have given still more information on the subject.

The literature of corrosion is rich in reference to the corrosion of iron and steel, but few of the papers have dealt with the microstructure of corroded specimens. Desch and Whyte[15] have studied the influence of manganese on the corrosion of steel, using the same methods as employed in studying the micro-chemistry of corrosion of brass and gun-metal, previously mentioned. Their results are inconclusive. Hadfield[16] believes that the microstructure of iron and steel has some effect on the kind and rate of corrosion.

LABORATORY TECHNIQUE FOR THE PREPARATION OF MICRO-SECTIONS.

MOUNTING OF SPECIMENS.

At the outset it should be pointed out that in reported papers the investigators seem to have totally ignored the difficulties which are encountered in preparing a suitable section of a corroded alloy for microscopic examination, and, therefore, a description of the technique involved seems fully warranted here. In carrying out the work, microscopic examination was made of sections from the original metals and alloys as submitted, and of the same materials after corrosion in mine water. In all, 52 metals and alloys, totalling about 150 test pieces, were corroded in water from the Edna No. 2 coal mine, and microscopic examination has been made of at least one specimen from each group. In addition, a few test pieces of special interest from tests in the Montour No. 1 mine were also examined under the microscope. The group of test pieces from the Edna No. 2 mine was chosen because the previous investigation, reported in Bulletin 4, had shown that, in general, the corrosion rate in this water was higher than the corrosion rates in the waters from the other mines.

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[12] Giolitti, F., and Ceccarelli, O., Sulla corrosione der bronze nelle soluzioni di electtroliti: *Gazz. Chem. Ital.*, vol. 39, 1909, Pt. 2, vol. VI, pp. 557-575.

[13] Merica, P. D., and Woodward, R. W., Failure of brass: 1—Microstructure and initial stress in wrought brass of the type 60 per cent copper and 40 per cent zinc: Bureau of Standards Tech. Paper 82, 1917, 72 pp.
Merica, P. D., Failure of brass: 2—Effect of corrosion on the ductility and strength of brass: Bureau of Standards Tech. Paper 83, 1916, 7 pp.
Merica, P. D., and Karr, C. P., Failure of brass: 3—Initial stress produced by the "burning in" of manganese bronze: Bureau of Standards Tech. Paper 84, 1916, 7 pp.

[14] Symposium, The failure of metals under internal and prolonged stress: A general discussion: Trans. Faraday Soc., vol. 27, Part I, December, 1921, pp. 2-2H.
Topical discussion on season and corrosion cracking of brass: Proc. Am. Soc. Test. Mat., vol. 18, Part 2, 1918, pp. 147-200.

[15] Desch, C. H., and Whyte, S., The influence of manganese on the corrosion of steel: *Jour.* West of Scotland Iron and Steel Inst., vol. 21, 1916, pp. 176-191.

[16] Hadfield, R. A., Corrosion of ferrous metals: Proc. Inst. of Civil Eng., vol. 214, Part 2, 1922, pp. 4-92.

Some of the corroded specimens had become very thin, and some were brittle; hence the problem of mounting them for polishing in such a way as to avoid further mechanical loss had to be solved. It was desired that the corroded edges of all the sections cut should be protected as far as possible from mechanical wear, while at the same time it was necessary that the sections be polished for etching and microscopic examination. The following method of mounting was adopted and used for all specimens, except a few where a larger section was desired than could be mounted in this way:

Sections were cut from ordinary galvanized steel pipe, 1 inch outside diameter and about ¾ inch in length. The specimens were cut approximately 1½ inches long by ½ inch wide. The thickness varied, depending on whether the section was original or corroded material, and whether rolled or cast. Figure 1 shows the approximate position of the sections cut from the original and corroded test pieces of rolled material. The section from the test piece was then placed in the pipe ring, and mounted by pouring liquid fusible alloy around the section. (A fusible alloy was used whose melting point was less than 200° C., to ensure that no burning or annealing of the sections should take place.)

In this manner a representative cross-section of each type of original and corroded material was mounted. Figure 2 is a photograph of a typical mounted specimen, showing the transverse cross-section of a thin test piece imbedded in fusible alloy. Where it was desired to mount a larger specimen than that which could be placed in the ring, use was made of a fiber-board mounting device, which consisted of two flat pieces of fiber board held together with screws. The specimen was placed between the boards, the edge which was to be examined being placed flush with parallel edges of the boards, and the screws then tightened to hold the specimen securely. The methods just described were found to be satisfactory in protecting the corroded edges during the grinding and polishing operations.

POLISHING.

The mounted sections were prepared for microscopic examination by grinding and polishing, using the orthodox methods of metallographers. Care was taken frequently to change the position of the specimen through an angle of 180 degrees, so as to avoid possible "flowing" of the metal.

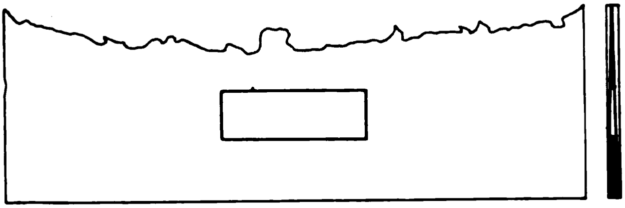

FIGURE 1.—*Elevation and end view of a typical corroded test piece showing approximate position of section cut for mounting for microscopic examination (half size).*

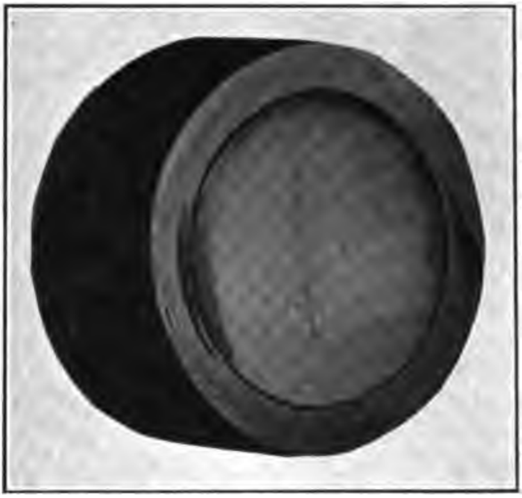

FIGURE. 2.—*End view of mounted specimen.*

ETCHING.

It is not necessary in the present bulletin to discuss in detail the etching of the different metals and alloys, although considerable difficulty was experienced in etching some alloys whose resistance to acid attack was high, and in etching coatings and corroded edges so as to bring out the characteristics of the corrosion attack. Etching reagents suitable for many metals and alloys have been described by Rawdon and Lorentz[17], and many of these were used in the present investigation. Other reagents that were found to be of value in this investigation, and not mentioned by Rawdon, are described later.

MICROSCOPIC EXAMINATION.

The results of the visual examination of the corroded metals and alloys have already been reported in Bulletin 4. Microscopic examination of the unetched specimens frequently revealed many points of interest, particularly in relation to pitting and the nature of the corroded edges and adhering coatings. These points will be dealt with when considering the illustrations. After etching, the specimens were examined at various magnifications and photographed at the lowest magnification which would show the features of interest. A photomicrographic record was made of all original and corroded specimens. Typical examples of specimens are shown in the accompanying illustrations. With each plate is given the designation, nominal composition, etch, and magnification for each figure shown, together with the mine water test-piece number, days immersed, and other data relating to the corrosion characteristics—where appropriate. The specimens were from rolled material, except where otherwise noted. Illumination was vertical, except for the macrographs, where oblique illumination was used.

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[17] Rawdon, H. S., and Lorentz, M. G., Metallographic etching reagents: I: for copper: Bureau of Standards Sci. Paper 399, 1920, 27 pp.

Rowdan, H. S., and Lorentz, M. G., Metallographic etching reagents: II: for copper alloys, nickel, and the alpha alloys of nickel: Bureau of Standards Sci. Paper 435, 1922, 41 pp.

FIGURE 3.—Admiralty metal, 70:29:1 Cu-Zn-Sn; grain size, 0.035 mm.; etch., $NH_4OH + H_2O_2$; X 100, original structure.

4.—Edge of Admiralty metal, 70:29:1 Cu-Zn-Sn; grain size, 0.035 mm.; test piece B-64, 35 days in Edna No. 2 mine water; etch, $NH_4OH + H_2O_2$; X 100.

5.—Edge of Admiralty metal, 70:29:1 Cu-Zn-Sn; grain size, 0.035 mm.; test piece B-66, 65 days in Edna No. 2 mine water; etch, $NH_4OH + H_2O_2$; X 100.

6.—Cross-section of Admiralty metal, 70:29:1 Cu-Zn-Sn; grain size, 0.025 mm.; test piece B-29, 65 days in Edna No. 2 mine water; etch, $NH_4OH + H_2O_2$; X 100.

7.—Cross-section of Admiralty metal, 70:29:1 Cu-Zn-Sn; grain size, 0.075 mm.; test piece B-69, 65 days in Edna No. 2 mine water; etch, $NH_4OH + H_2O_2$; X 100.

8.—Low brass (with copper nodules), 80:20 Cu-Zn; test piece A-20, 119 days in Montour No. 1 mine water; etch, $NH_4OH + H_2O_2$; X 100.

Discussion.—The specimens of Admiralty metal shown in the photomicrographs are of the alpha type of brass. Figures 4 and 5 illustrate the effect of variation in the time of exposure to the mine water, the ridges shown being those between shallow elongated pits. (See Bull. 4, Table 7, column 5.) It will also be noted that specimens of the same composition, exposed for the same time-period, but varying in grain size, are shown. Data of actual loss in weight showed that the pieces of Admiralty metal of smaller grain size corroded slightly faster than those of the larger grain size, but the difference is small. Figure 8 shows a nodule of re-deposited copper on the surface of low brass.

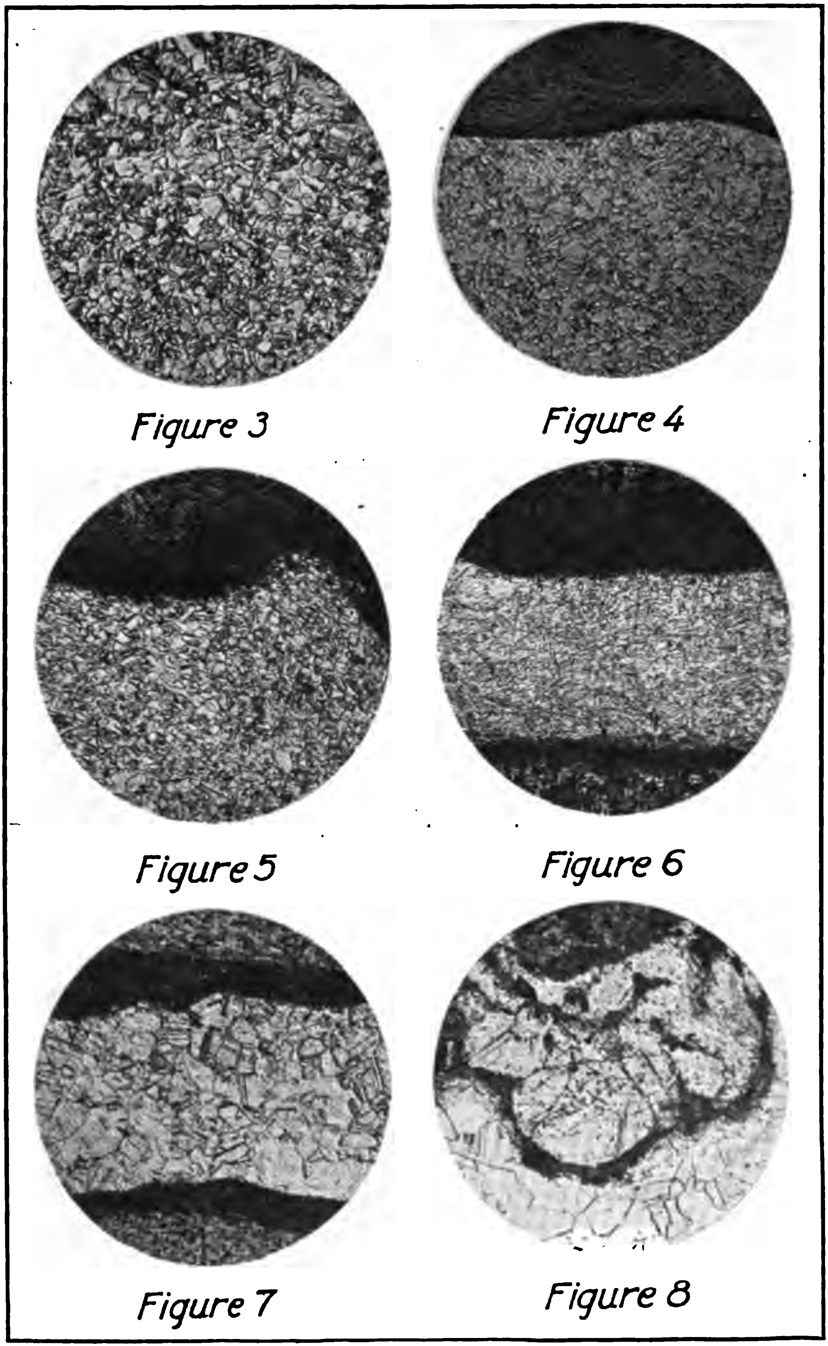

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Plate I.—*Structure of original and corroded test pieces.*

FIGURE 9.—Cross-section of low brass, 80:20 Cu-Zn; test piece B-20, 65 days in Edna No. 2 mine water, etch, $NH_4OH+H_2O_2$; X 100.

10.—Copper; etch, $NH_4OH+H_2O_2$; X 100.

11.—Cross-section of copper, test piece B-27, 65 days in Edna No. 2 mine water; etch, $NH_4OH+H_2O_2$; X 100.

12.—Naval brass, 60:39:1 Cu-Zn-Sn; 65 days in Edna No. 2 mine water; etch, $NH_4OH+H_2O_2$; X 100. Corrosion products on edge of piece are shown.

13.—Naval brass, 58:41:0.5:0.5 Cu-Zn-Sn-Fe; etch, $NH_4OH+H_2O_2$; X 200, original structure.

14.—Naval brass, 58:41:0.5:0.5 Cu-Zn-Sn-Fe; 72 days in Edna No. 2 mine water; etch, $NH_4OH+H_2O_2$; X 100.

Discussion.—Figure 9 shows a cross-section of low brass corroded in the Edna No. 2 mine water, which, unlike the same material corroded in Montour No. 1 mine water, shows no deposited copper nodules. Figures 10 and 11 are photomicrographs of commercially pure copper, the latter showing the thin cross-section, after corrosion. Figure 12 gives an excellent example of selective corrosion, the beta (zinc-rich) constituent has been corroded, leaving the alpha (light-colored crystals) relatively uncorroded. Figure 13 shows the original structure of a bronze of similar composition, while Figure 14 again shows a case of selective corrosion of alpha-and-beta brass.

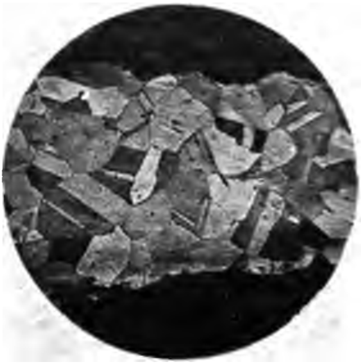

Figure 9

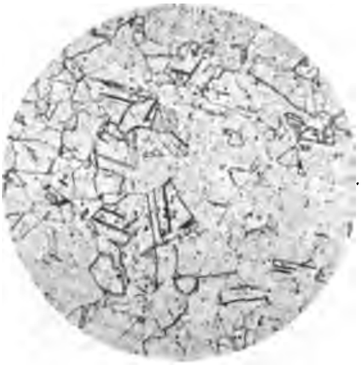

Figure 10

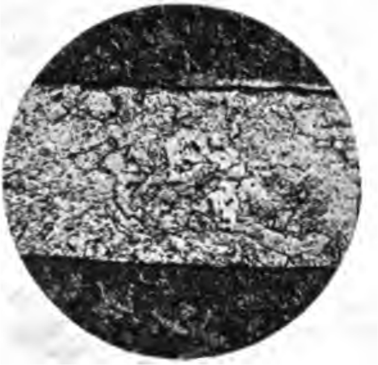

Figure 11

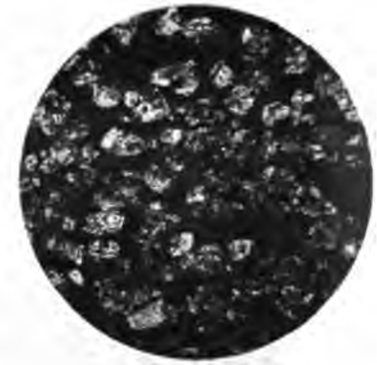

Figure 12

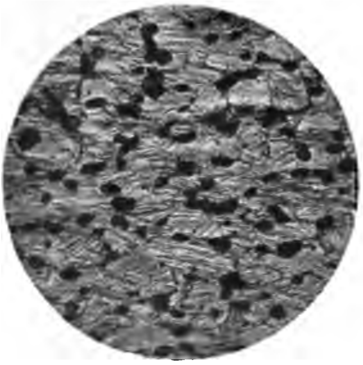

Figure 13

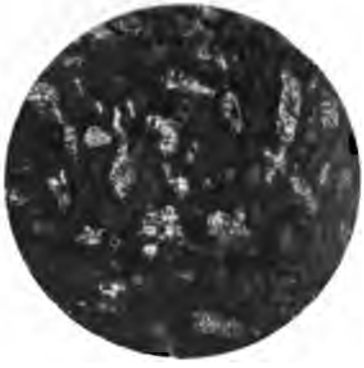

Figure 14

Plate II.—*Structure of original and corroded test pieces.*—Continued.

FIGURE 15.—Cross-section manganese brass, 68:28:2:2 Cu-Zn-Fe-Mn; test piece B-152, 72 days in Edna No. 2 mine water; not etched; X 2; oblique illumination.

16.—Cross-section cast manganese brass, 68:28:2:2 Cu-Zn-Fe-Mn; test piece B-145, 72 days in Edna No. 2 mine water; not etched; X 2; oblique illumination.

17.—Manganese brass, 68:29:2:1 Cu-Zn-Mn-Fe; test piece B-148, 72 days in Edna No. 2 mine water; etch, $NH_4OH+H_2O_2$ and acidic $FeCl_3$; X 300.

18.—Manganese brass, 66:31:2:1 Cu-Zn-Mn-Fe; test piece B-151, 72 days in Edna No. 2 mine water; etch, $NH_4OH+H_2O_2$ and acidic $FeCl_3$; X 300.

19.—Manganese brass, 66:31:2:1 Cu-Zn-Mn-Fe; original structure; etch, $NH_4OH+H_2O_2$ and acidic $FeCl_3$; X 300.

20.—Cast manganese brass, 68:28:2:2 Cu-Zn-Fe-Mn; original structure; etch, $NH_4OH+H_2O_2$ and acidic $FeCl_3$; X 300.

Discussion.—Figures 15 and 16 show a peculiar phenomenon—, the very even re-deposition of copper on manganese brass after corrosion. The dark areas on the outer edges are copper-rich, varying in composition from 85 to 95 per cent copper, according to the points from which samples were taken. The light central areas are uncorroded brass. Figures 17 and 18 show the grain boundaries retained from original structure in the corrosion product, or re-deposited copper. The straight line in Figure 17 marks the junction of the corrosion attack from both sides of the test piece. None of the original brass remains. Figures 19 and 20 show the typical original structure of rolled and cast manganese brass.

Figure 15

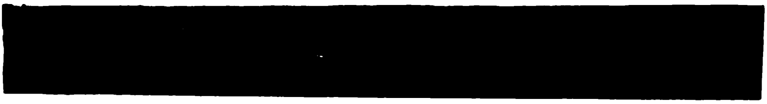

Figure 16

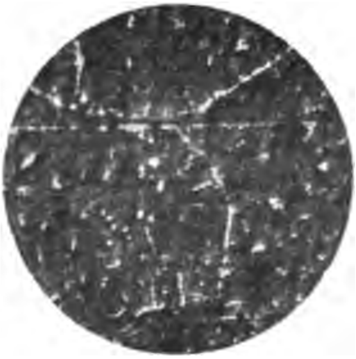

Figure 17

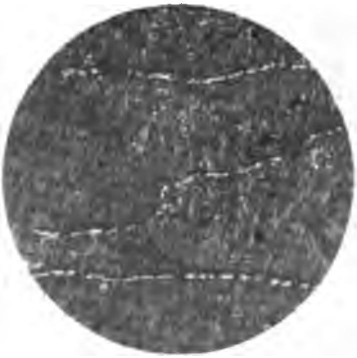

Figure 18

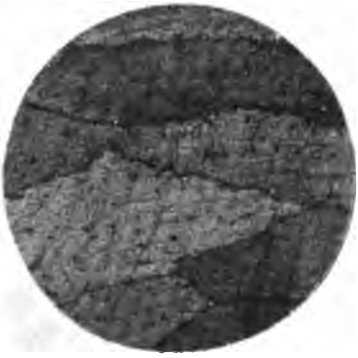

Figure 19

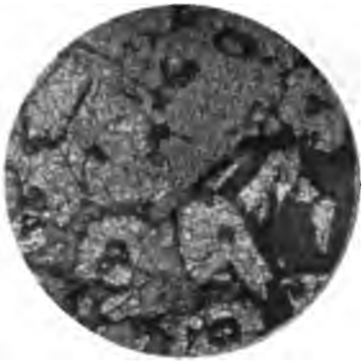

Figure 20

PLATE III.—*Structure of original and corroded test pieces.*—Continued.

FIGURE 21.—Corroded edge, cast manganese brass, 68:28:2:2 Cu-Zn-Fe-Mn; test piece B-145, 72 days in Edna No. 2 mine water; etch, $NH_4OH+H_2O_2$ and acidic $FeCl_3$; X 300.

22.—Cast manganese brass, 68:28:2:2 Cu-Zn-Fe-Mn; test piece B-145, 72 days in Edna No. 2 mine water; etch, $NH_4OH+H_2O_2$ and acidic $FeCl_3$; X 300.

23.—Cast bronze, 90:10 Cu-Sn; etch, acidic $FeCl_3$; X 300.

24.—Cast bronze, 90:10 Cu-Sn; test piece B-80, 135 days in Edna No. 2 mine water; etch, acidic $FeCl_3$; X 300.

25.—Cast leaded bronze, 88:10:2 Cu-Sn-Pb; etch, acidic $FeCl_3$; X 300.

26.—Cast leaded bronze, 88:10:2 Cu-Zn-Pb; test piece B-83, 135 days in Edna No. 2 mine water; etch, acidic $FeCl_3$; X 300.

Discussion.—Figure 21 shows the structure of the coating on test piece B-145, near the edge. The nodular masses, one of which is marked *A*, are copper crystals which have evidently grown from solution. Figure 22 shows the microstructure of the corroded edge of the same specimen (B-145) nearer the uncorroded portion. The light-colored crystals are apparently the same as shown in Figure 20, which showed the original structure. Figure 23 shows original structure of the 90:10 Cu-Sn bronze with casting strain lines and coring of the delta. After corrosion, a coating or layer can be observed on the edge, seemingly built up along the delta stringers, as shown in Figure 24. Figure 25 shows original structure of the cast-leaded bronze, and Figure 26 shows a coating similar to that shown in Figure 24.

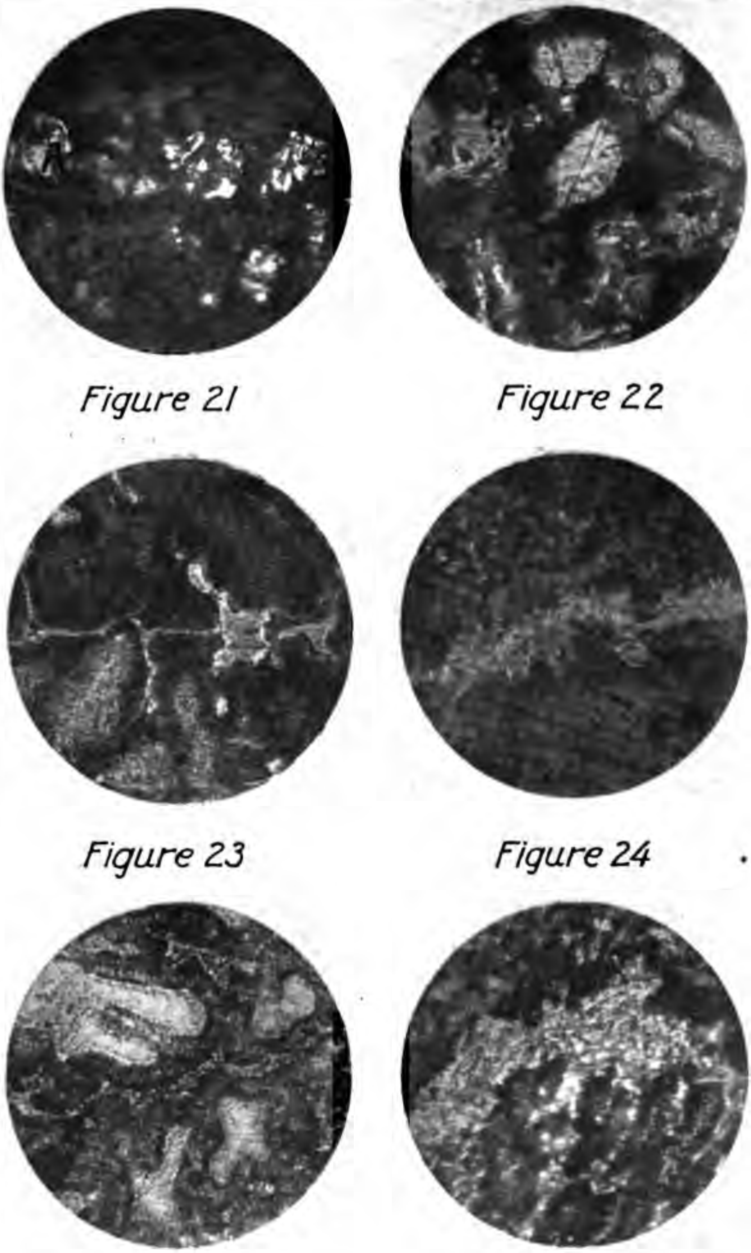

Figure 21

Figure 22

Figure 23

Figure 24

Figure 25

Figure 26

Plate IV.—*Structure of original and corroded test pieces.*—Continued.

FIGURE 27.—Panoramograph of a cross-section of hard-rolled phosphor-bronze, 90:4.5:5.4:0.1 Cu-Pb-Sn-P; test piece B-50, 135 days in Edna No. 2 mine water; etch, $NH_4OH + H_2O_2$ and $FeCl_3$; original magnification, X 200; reduced one-third in half-tone.

Discussion.—The original structure, corrosion edges, and coatings are shown. It will be noted that the nodules of lead (black dots) remain in the coating, which is evidently of the protective type. The piece was cleaned in the usual manner, and the coating shown is that left after cleaning.

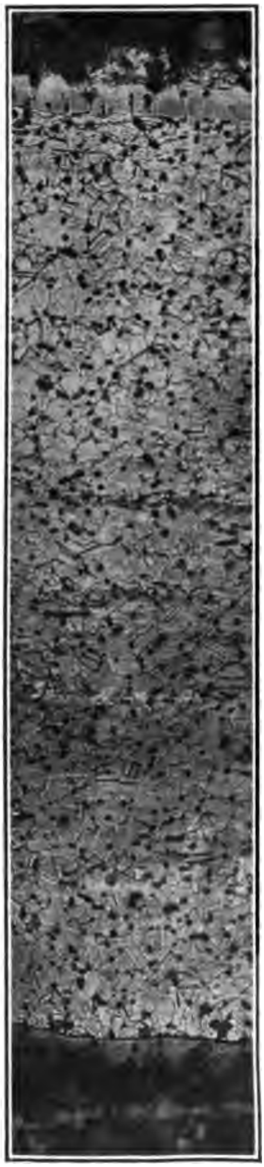

Plate V, Figure 27.—*Panoramograph of test piece B-50 after corrosion (reduced one-third).*

FIGURE 28.—Cast leaded bronze, 75:15:10 Cu-Pb-Sn; etch, acidic $FeCl_3$; X 300; original structure.

29.—Cast leaded bronze, 75:15:10 Cu-Pb-Sn; test piece B-87, 135 days in Edna No. 2 mine water; etch, acidic $FeCl_3$; X 300.

30.—Cupro-nickel, 85:15 Cu-Ni; etch, 20 per cent aqueous HNO_3; X 100; original structure.

31.—Cross-section cupro-nickel, 85:15 Cu-Ni; test piece B-32, 65 days in Edna No. 2 mine water; etch, 20 per cent aqueous HNO_3; X 100.

32.—Cast iron-chromium-silicon cupro-nickel, 42:35:12:9:2 Cu-Ni-Cr-Fe-Si; test piece B-5, 135 days in Edna No. 2 mine water; etch, 20 per cent aqueous HNO_3; X 100.

33.—Cast leaded cupro-nickel, 54:25:20:0..5:0..5 Cu-Ni-Pb-Sn-Fe; test piece B-2, 135 days in Edna No. 2 mine water; etch, aqueous HNO_3 and acetic acid; X 100.

Discussion.—Figure 28 shows the original structure of a heavily leaded bronze. Figure 29 again illustrates that the delta of the bronzes is the most resistant material, as shown by the preponderance of delta on the corrosion edge. Rolled 15 per cent cupro-nickel corrodes rapidly, the corroded piece becoming very thin but does not pit, as shown by Figure 31. Corrosion edges of complex cupro-nickels are shown in Figures 32 and 33. The last two mentioned cupro-nickels are more resistant to corrosion by mine water than is ordinary cupro-nickel.

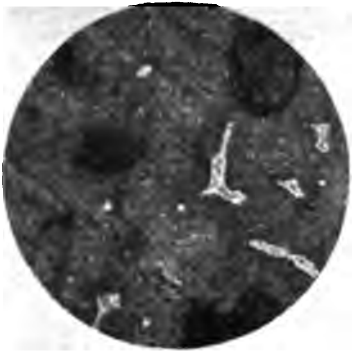

Figure 28

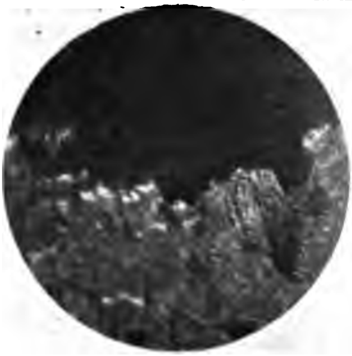

Figure 29

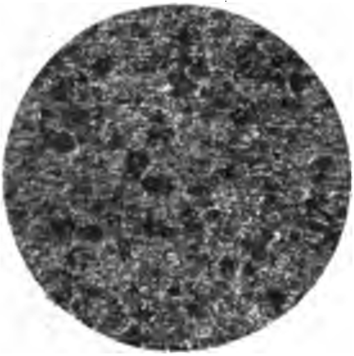

Figure 30

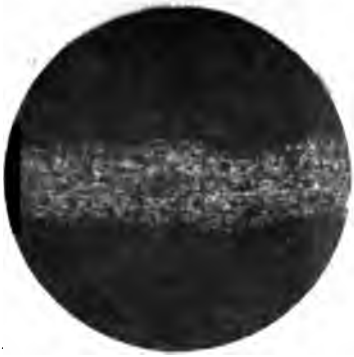

Figure 31

Figure 32

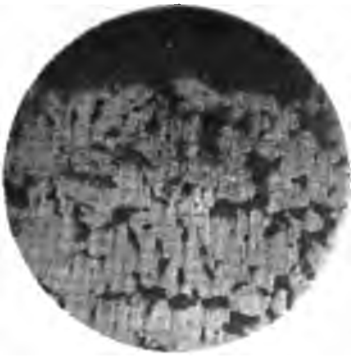

Figure 33

PLATE VI.—*Structure of original and corroded test pieces.*—Continued.

FIGURE 34.—Lead-tin-nickel silver, 63.5:13:11.5:7.5:4.5 Cu-Ni-Zn-Pb-Sn; test piece B-8, 135 days in Edna No. 2 mine water; etch, $NH_4OH+H_2O_2$; X 100.

35.—Cross-section of nickel silver, 64:18:18 Cu-Zn-Ni; test piece B-14, 65 days in Edna No. 2 mine water; etch, HNO_3+FeCl_3; X 100.

36.—Nickel silver, 53:34:13 Cu-Zn-Ni; test piece B-35, 65 days in Edna No. 2 mine water; etch, $NH_4OH+H_2O_2$; X 100.

37.—Cross-section of nickel silver, 66:24:10 Cu-Zn-Ni; test piece B-44, 51 days in Edna No. 2 mine water; etch, $NH_4OH+H_2O_2$; X 100.

38.—Commercially pure aluminum; test piece B-109, 21 days in Edna No. 2 mine water; not etched; X 2.

39.—Aluminum alloy, duralumin type, 3.5:0.5:0.5:0.5 Cu-Fe-Mn-Si, remainder Al; test piece B-98, 51 days in Edna No. 2 mine water; not etched; X 300.

Discussion.—A group of corroded edges of four nickel silvers, varying considerably in chemical composition, is shown in Figures 34 to 37. The piece shown in Figure 34 was the most resistant of the nickel silvers to acid mine water attack, but none of the nickel silvers can be classed as corrosion-resisting for service in acid mine water. Figure 38 is a macrograph of commercially pure aluminum, showing the deep, elongated pits formed. All kinds of aluminum alloys pitted when tested, but the pitting characteristics of the alloys differ among themselves and from the characteristic pitting of commercially pure aluminum. Figure 39 shows pits formed in an aluminum alloy, observed at a magnification of 300 diameters.

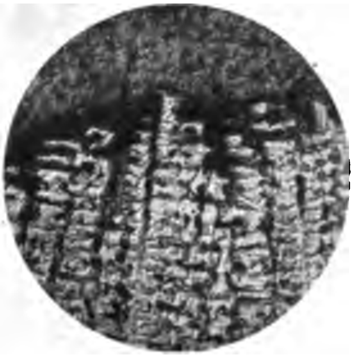

Figure 34

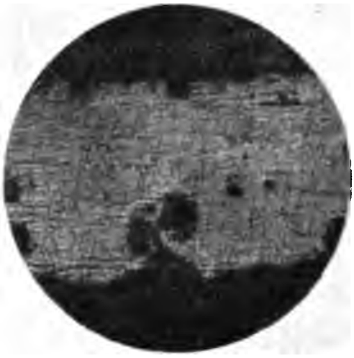

Figure 35

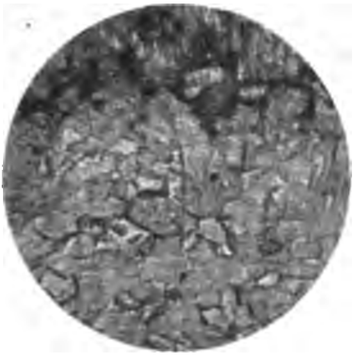

Figure 36

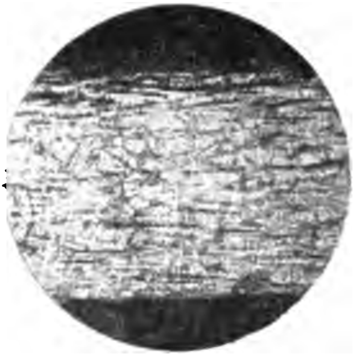

Figure 37

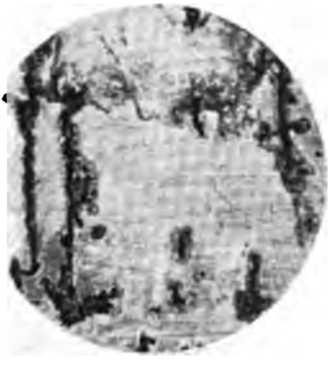

Figure 38

Figure 39

Plate VII.—*Structure of original and corroded test pieces.*—Continued.

FIGURE 40.—Cast aluminum alloy, 95:5 Al-Si; test piece B-89, 72 days in Edna No. 2 mine water; not etched; X 5; oblique illumination.

41.—High-silicon cast iron—Si, 14.0; C, 0.8; etch, HNO_3+HF; X 300.

42.—Cross-section of pure ingot iron—Fe, 99.9; test piece B-116, 35 days in Edna No. 2 mine water; etch, 20 per cent aqueous HNO_3; X 300.

43.—High-silicon cast iron—Si, 14.5; C, 1.5; etch, HNO_3+HF; X 300.

44.—High-silicon cast iron—Si, 14.5; C, 1.5; test piece B-132, 35 days in Edna No. 2 mine water; etch, HNO_3+HF; X 300.

Discussion.—In Figure 40 is shown part of a cross-section of a corroded cast Al-Si alloy. The deep pitting is clearly shown. Figure 42 shows a cross section of commercially pure iron, which had been rapidly corroded. Figure 41 shows the typical structure of a high-silicon cast iron. As would be expected from the extremely low loss in weight of this group (No. 133, 134, 135), no change could be observed on the edges or faces of pieces after corrosion. Figure 43 shows typical structure of another high-silicon cast iron. Test pieces of this group (No. 130, 131, 132), did corrode to an appreciable extent, the corrosion edge of one piece being shown in Figure 44. There is a difference in the method of melting and also in the carbon content of these two high-silicon cast irons.

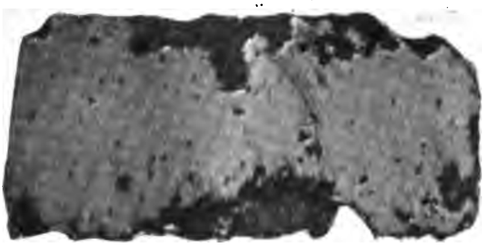

Figure 40

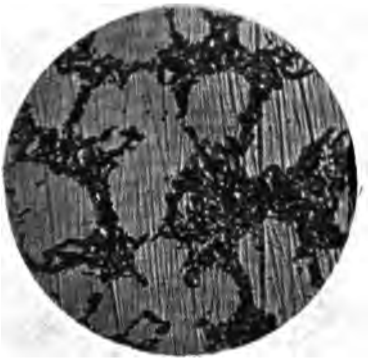

Figure 41

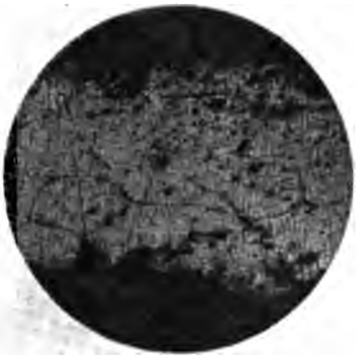

Figure 42

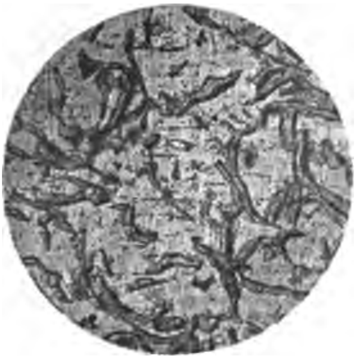

Figure 43

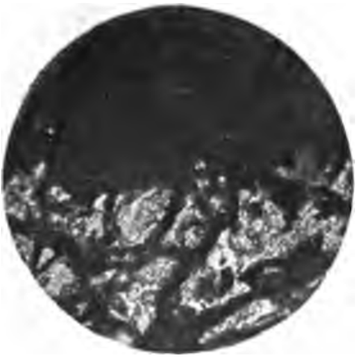

Figure 44

PLATE VIII.—*Structure of original and corroded test pieces.*—Continued.

FIGURE 45.—High-chromium steel—Cr about 30 per cent, and C, Si, Mn, S, low; X 300; etch, Kourbatoff's solution (this consists of 5 c. c. of con. HCl, 20 c. c. of iso-amyl alcohol, and 9 c. c. saturated solution of picric acid in alcohol).

46.—Cr-Ni-Si steel—24:13:3.5 Ni-Cr-Si, remainder Fe, with C, Mn, and S, low; etch, Kourbatoff's solution; X 300.

47.—Monel metal—65:31:4 Ni-Cu-Fe; test piece B-41, 79 days in Edna No. 2 mine water; etch, con. HNO_3; X 300.

48.—Lead-copper alloy—50:50 Pb-Cu; test piece B-72, 121 days in Edna No. 2 mine water; not etched; X 5; oblique illumination.

49.—Cast high-lead alloy—96% Pb, remainder alkaline earth metals; test piece B-154, 72 days in Edna No. 2 mine water; not etched; X 2; oblique illumination; side view.

50.—Cast high-lead alloy—96% Pb, remainder alkaline earth metals; test piece B-154, 72 days in Edna No. 2 mine water; not etched; X 2; oblique illumination; end view.

Discussion.—Figure 45 shows the microstructure of a high-chromium steel, and Figure 46 the microstructure of a chromium-nickel-silicon steel. As neither of these alloys corroded to any appreciable extent, no attempt is made to show corrosion edges. The corroded edge of a specimen of monel metal is shown in Figure 47. In the lead-copper alloy shown in Figure 48, the copper was corroded more rapidly than the lead, and the resulting pits can be noted. A high-lead alloy, while actually gaining weight in the corrosion test, "blistered" and "cracked", as shown in the side and end views—Figures 49 and 50.

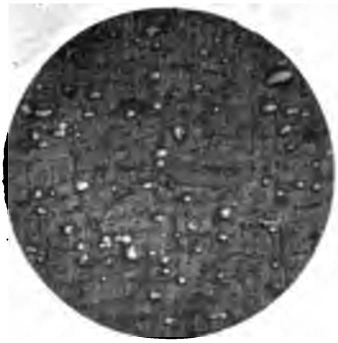

Figure 45

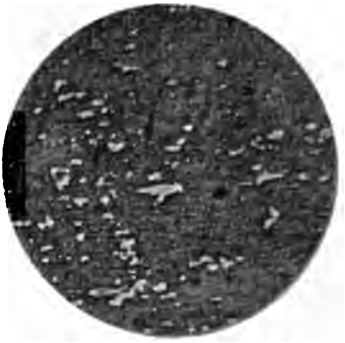

Figure 46

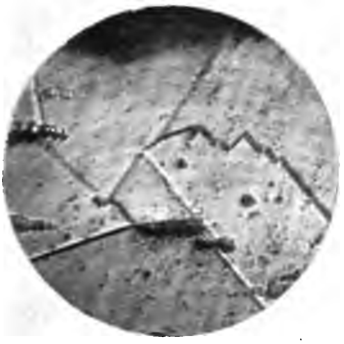

Figure 47

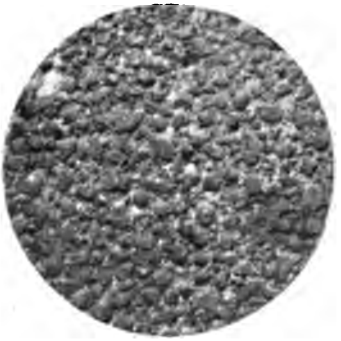

Figure 48

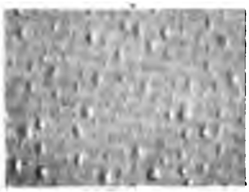

Figure 49

Figure 50

PLATE IX.—*Structure of original and corroded test pieces.*—Continued.

SUMMARY AND CONCLUSIONS.

In summing up the work described here, the following conclusions have been drawn:

1. In brasses, the grain size seems to have little, if any, effect upon the rate or nature of the corrosion.
2. In alloy systems where two or more phases are present, there is usually, although not necessarily, one phase that is more resistant to corrosion than the other phases. This gives rise to the phenomenon of selective corrosion. In bronzes, the delta is the more resistant phase; while in alpha-beta brass, the alpha is the more resistant.
3. The other alloys tested were of such types that selective corrosion did not take place, or if it did, the constituent first corroded could not be ascertained. Of the other groups, the brasses not previously mentioned fall within the alpha phase, as do the nickel silvers. The cupro-nickels have only one phase, because copper and nickel form solid solutions in all proportions. In alloys containing four or more components, so little work has been done with the constitutional diagrams that it is not possible to ascertain the conditions of thermal equilibria, hence, in most cases, it can not be accurately stated which phase or constituent is first attacked.
4. Aluminum and aluminum alloys pit so badly that selective corrosion can not be identified as such. The pits seem to be caused, in rolled material, by the condition brought about by cold work rather than by the constituents that may be present.
5. Some alloys, which, after corrosion and subsequent cleaning appear to be free from adhering coating or precipitate, have a very hard and probably quite impervious coating acting as a protection; this is particularly true of the bronzes.
6. Corrosion attack does not, in general, follow grain boundaries, but proceeds through the less resistant material if two or more phases be present. The more resistant material is probably removed, as such, after the less resistant material has been corroded and washed away. In one component systems, attack apparently proceeds without reference to grain boundaries, which view is not in complete agreement with some investigators, notably Desch[18], and the statements here made can only be taken to apply to corrosion by acid mine water.
7. Microscopic study of the corrosion resisting high-silicon iron, high-chromium steel, chromium-nickel-silicon steels and nichrome reveals no visible protecting coating or film. The resistance

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[18] Desch, C. H., Physical and mechanical factors in corrosion: Trans. Faraday Soc., vol. 11, 1916, pp. 198-203.

to corrosion of these alloys can probably be traced to their chemical composition. It is true, however, that the physical properties resulting from the method of manufacture have an important effect on the retarding of the corrosion rate. It is known that iron silicide and the double carbide of iron and chromium are very insoluble in acids.

Study has not yet been made of very thin coatings or films, nor has study of the thicker coatings—protective and otherwise—been completed. Some data have been accumulated, and further research on the film problem is in progress. Laboratory experiments are contemplated to determine the nature and extent of films that are of ultra-microscopic thickness, but which may be protective.

APPENDIX

SUPPLEMENT TO BULLETIN 4.

CORROSION TESTS ON METALS AND ALLOYS IN ACID MINE WATERS FROM COAL MINES.

As mentioned in the foregoing pages, previous work on the corrosion losses in acid mine water was published in Bulletin 4[1], and as some tests have since been made on other alloys, the results are given in the following pages.

A series of 10 alloys was immersed in flowing mine water at the Edna No. 2 mine of the Hillman Coal & Coke Co., at Wendel, Westmoreland County, Pa. Conditions of the test were maintained as nearly as possible like those of the previous test, to which the reader is referred for details.

SUMMARY OF METHOD OF TESTING.

The test pieces had the following approximate dimensions: Rolled materials, 2 by 6 inches by 16 (B&S) gage, equal to 0.05 inch; and cast materials, 2 by 6 by ¼ inch. The pieces were weighed, measured, immersed, and at the conclusion of the tests were cleaned, dried, and weighed.

The apparatus used was the same as that in the previous test, and the control of water flow was regulated to 1.8 inches per minute. Analysis of the water was also made in the same way. The results are given in Tables 1 and 2.

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[1] Selvig, W. A., and Enos, George M., Corrosion tests on metals and alloys in acid mine waters from coal mines: Bull. 4, Carnegie Institute of Technology, 1922, 71 pp.

TABLE 1.—*Composition, days immersed, average free and total acidity of water, and loss in weight of test pieces exposed to action of mine water from Edna No. 2 mine.*

Designation.	Chemical composition, per cent.	Test piece number.	Average loss in milligrams per sq. cm. per day.	Average free acidity. in p. p. m.[b]	Average total acidity. in p. p. m.[c]	Days immersed.
Cast manganese brass	Cu, 68.05 Mn, 2.06 Pb, 0.45 Zn, 27.89 Fe, 1.55	142, 143, 144	3.29	2260	10,420	72
Cast manganese brass	Cu, 67.45 Pb, 0.28 Zn, 28.84 Mn, 1.95 Fe, 1.48	145, 146, 147	3.64	2260	10,420	72
Rolled manganese brass	Cu, 67.10 Pb, 0.30 Zn, 29.64 Mn, 1.99 Fe, 0.97	148, 149, 150	4.49	2260	10,420	72
Rolled manganese brass	Cu, 65.5 Pb, 0.5 Zn, 30.5 Mn, 2.2 Fe, 1.3	151, 153	4.13	2260	10,420	72
Cast lead alloy	Pb, 96.1 Alkaline earth metals, remainder	154, 155, 156	+0.67	2260	10,420	72
Copper-lead alloy	Cu, 68.0 Pb, 31.9	157, 159	4.86	2070	13,480	65

TABLE 1.—*Composition, days immersed, average free and total acidity of water, and loss in weight of test pieces exposed to action of mine water from Edna No. 2 mine.*—Continued.

Designation.	Chemical composition, per cent.	Test piece number.	Average loss in milligrams per sq. cm. per day.	Average free acidity. in p. p. m.[b]	Average total acidity. in p. p. m.[c]	Days immersed.
Copper-lead alloy	Cu, 73.01 Pb, 26.96	160, 161	4.77	2070	13,480	65
Rolled manganese bronze, coated with protective paint	Cu, 65.5 Pb, 0.5 Zn, 30.5 Mn, 2.2 Fe, 1.3	151, 152	0.074	2070	13,480	65
Rolled pure iron, coated with protective paint	Fe[a], 99.9	115, 116	0.914	2070	13,480	65
Rolled Naval brass, coated with protective paint	Cu[a], 60.40 Zn, 38.83 Sn, 0.77	22, 23	0.091	2070	13,480	65

[a] The analyses given were furnished by the co-operating companies.

[b] Free acidity is expressed in parts per million of sulphuric acid, and is the acidity due to free sulphuric acid.

[c] Total acidity is expressed in parts per million of sulphuric acid, and is the acidity due to free sulphuric acid, plus sulphates of iron and aluminum.

TABLE 2.—*General appearance of test pieces at conclusion of corrosion tests in acid mine water from Edna No. 2 mine.*

Designation.	Approximate chemical composition, per cent.	Test piece number.	Appearance.
Cast manganese brass	Cu, 63.05 Pb, 0.45 Zn, 27.89 Mn, 2.06 Fe, 1.55	142, 143, 144	A hard, metallic, brittle coating formed. Corrosion progressed evenly and to about one-fourth the thickness of the specimen. Coating practically all copper.
Cast manganese brass	Cu, 67.45 Pb, 0.28 Zn, 28.84 Mn, 1.95 Fe, 1.48	145, 146, 147	A hard, metallic, brittle coating formed. Corrosion progressed evenly and to about one-fourth the thickness of the specimen. Coating practically all copper.
Rolled manganese brass	Cu, 67.10 Pb, 0.30 Zn, 29.64 Mn, 1.99 Fe, 0.97	148, 149, 150	A hard, copper-rich coating formed. Corrosion progressed evenly to about two-thirds the thickness of the specimen. Coating easily split off.
Rolled manganese brass	Cu, 65.5 Pb, 0.5 Zn, 30.5 Mn, 2.2 Fe, 1.3	151, 153	Corrosion penetration practically complete. The piece retained original form, but only the copper-rich coating remained.
Cast lead alloy	Pb, 96.1 Alkaline earth metals, remainder	154, 155, 156	The surface of the metal showed blisters. No visible coating. Pieces developed cracks at ends.
Cast copper-lead alloy	Cu, 68.0 Pb, 31.9	157, 159	The pieces had a grey coating which could be removed with difficulty. Considerable uniform corrosion.

TABLE 2.—*General appearance of test pieces at conclusion of corrosion tests in acid mine water from Edna No. 2 mine.*—Concluded.

Designation.	Approximate chemical composition, per cent.	Test piece number.	Appearance.
Cast copper-lead alloy	Cu, 73.01 Pb, 26.95	160, 161	The pieces had a grey coating which could be removed with difficulty. Considerable uniform corrosion.
Rolled manganese brass, coated with protective paint	Cu, 65.5 Pb, 0.5 Zn, 30.5 Mn, 2.2 Fe, 1.3	151, 152	The paint retarded corrosion. No visible coating from mine water action.
Rolled pure iron, coated with protective paint	Fe[a], 99.9	115, 116	The paint retarded corrosion. Many pits had started. Some irregular corrosion.
Rolled Naval brass, coated with protective paint	Cu, [a]60.40 Zn, 38.83 Sn, 0.77	22, 23	The paint retarded corrosion. No visible coating from mine water action.

[a] The analyses given were furnished by the co-operating manufacturers.

DISCUSSION OF RESULTS.

Manganese brass.—The actual loss in weight of the manganese brasses, test pieces No. 142 to 153, inclusive, is comparable with the loss in weight of some bronzes corroded under similar conditions, This group, however, is characterized by a peculiar kind of coating formed during the corrosion process. The coating is decidedly metallic, the copper content being approximately 95 per cent in the case of the rolled material. The coating adheres rather tightly, but can be chipped off as it is rather brittle.

Macrographs of typical specimens are shown in Figures 13 and 14, and micrographs are shown in Figures 16 to 20. As the original composition of the manganese brasses shows a copper content of approximately 65 to 67 per cent, the probable explanation of the phenomenon may be stated as follows: The corrosion of copper and zinc proceeds uniformly, but the potential of the original alloy is such that the copper is re-deposited in a porous mass from the mine water, while the zinc remains in solution. The deposited copper does not hinder further corrosion. The mechanism of the corrosion, as shown by the microstructure of the corroded specimens, has been discussed on page 20. It may be further noted that the pieces retained their original shape, even when practically all that remained was the corrosion product— that is, re-deposited copper.

High lead alloys.—The alloy containing 96.1 per cent lead—test pieces No. 154, 155, and 156—showed a slight increase in weight, indicating either that the metal was porous and absorbed deposited salts, or that a coating was formed which weighed more than the material lost in the corrosion process, or possibly a combination of both causes. As shown in the macrographs (Figures 49 and 50), the surface has a blistered appearance, while the ends developed large cracks. The copper-lead alloys corroded in a uniform manner. As is known, copper and lead are insoluble in all proportions in the solid state, and it is not usual to find uniform corrosion in a copper-lead alloy as the copper tends to dissolve first, causing pitting, as is shown in Figure 48. Test pieces No. 157, 159, 160, and 161, show a corrosion loss comparable with the loss of ordinary bronzes, and are not pitted to any great extent.

EXPERIMENTS WITH PROTECTIVE COATINGS.

It was desired to ascertain whether a good grade of paint—that is, an artificial protective coating—would retard the rate of corrosion. Duplicates of test pieces from former tests were chosen

—namely, pure iron, Naval brass, and a manganese brass—and were numbered the same as before. A coal-tar paint of good quality and reputed to be corrosion-resisting was chosen, and applied to the test pieces which had not been polished. The pieces were then dried and weighed and tested under the usual conditions.

Very little corrosion loss took place in the specimens of brass and bronze. While the corrosion was retarded in the case of iron, the loss was considerable, and pitting had also taken place. It is possible that adhering mill scale did not permit the paint to adhere tightly to the iron, thus allowing openings through the coating for the mine water to attack the metal.

SUMMARY.

1. Ten alloys, three of which had artificial protective coatings; were subjected to the action of acid mine water in the same manner as described in Bulletin 4[2].

2. The tests covered a period of between two and three months. Average free and total acidity of the water, average loss in weight in milligrams per square centimeter per day and composition of the test pieces are given in Table 1, and the nature of the corrosion is noted in Table 2, of the Appendix.

3. The corrosion of a group of manganese brasses, two copper-lead alloys, a high-lead alloy, and a group of test pieces with artificial protective coatings has been discussed and conclusions noted.

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[2] Work cited.

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Bulletin 6

COAL-MINING INVESTIGATIONS

UNDER AUSPICES OF

CARNEGIE INSTITUTE OF TECHNOLOGY,
U. S. BUREAU OF MINES, AND
ADVISORY BOARD OF COAL-MINE OPERATORS AND ENGINEERS.

ACCELERATED CORROSION TESTING OF METALS AND ALLOYS IN ACID MINE WATER

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PREFACE.

Pittsburgh is the greatest industrial center in America, and the heart of the greatest bituminous coal-mining district in the world. It is eminently desirable, therefore, that this city should have an institution which devotes a part of its great facilities to the scientific study of that branch of the industry which is largely responsible for Pittsburgh's development and that of western Pennsylvania.

On May 27, 1919, a number of leading representatives of the coal-mining industry of western Pennsylvania met in conference with the President of Carnegie Institute of Technology with a view of bringing about closer relations between the Institute and the mining interests. It was felt that the advice and co-operation of men in the field were necessary for the training of young men for mining work, and at the conclusion of the meeting the following resolution was adopted:

> That this gathering give its approval and moral and material support to the form of education proposed for the Carnegie Institute of Technology by which students may receive a combined technical, practical, and business training, necessary to fit them for service in the coal mining and allied industries. Further, that the President of the Carnegie Institute of Technology appoint a board of no less than ten men representing the coal mining and allied industries, the United States Bureau of Mines, the State Department of Mines, and the Carnegie Institute of Technology, who will advise and assist in carrying out this program of education and training, particularly in its practical phases to the mining industry and in its co-operation with the United States Bureau of Mines.

Following further the intention of this resolution, the President of the Institute entered into a co-operative agreement on June 1, 1919, with the Director of the U. S. Bureau of Mines whereby full advantage could be taken of the Bureau's laboratories, equipment, and library, as well as of the advice and instruction of its technical staff.

To carry out this new program there was organized during the summer months the Co-operative Mining Courses in the Department of Mining and Metallurgical Engineering, College of Engineering, of the Institute. The course in mining engineering covers four years, and leads to the degree of Bachelor of Science. The two-year course in coal mining is planned to prepare men

with a certain amount of practical experience for executive positions. The four-weeks intensive summer course in coal mining is designed for miners who aspire to be firebosses and mine foremen.

In a large measure, the new mining, ore-dressing, and coal-washing laboratories at the Institute have been equipped gratuitously by various manufacturers of mining machinery and appliances. Co-operative research through teaching and research fellowships is devoted to various problems in coal mining and the utilization of fuels. The Institute selects the fellows, the Bureau of Mines provides the laboratory facilities, and the Advisory Board determines what problems be undertaken, and publishes the reports.

The primary object of this co-operation of the Carnegie Institute of Technology, the U. S. Bureau of Mines, and the Advisory Board of Coal Mine Operators and Engineers is the proper education and training of young men for the mining industry. The ultimate objective is to bring about better conditions and greater efficiency in mining operations. The decrease in reserves of coal and increasing cost of production make it urgently necessary for mine operators and engineers to take advantage of everything which modern science, machinery, and methods can contribute.

EDWARD STEIDLE,
Supervisor, Co-operative Mining Courses,
Carnegie Institute of Technology.

FOREWORD.

The investigation described in this paper was conducted by the Co-operative Mining Courses, Department of Mining, Carnegie Institute of Technology, and the Pittsburgh Experiment Station of the U. S. Bureau of Mines, in co-operation with the coal-mining industry of western Pennsylvania. Under co-operative agreement, four research fellowships paying $750 per annum per year of ten months, are supported by the Carnegie Institute of Technology. These fellowships are open to properly qualified graduates of universities and technical schools. The research work is carried on in the laboratories of the Bureau of Mines, under the direction of one or more members of the Bureau research staff, and is published under the joint authorship of the investigators.

Fellowship holders are required to register at the Institute as graduate students, and become candidates for the degree of Master of Science, unless an equivalent degree has been previously earned. The purpose of these fellowships is the solution of problems in mining and the utilization of coal.

This bulletin describes an accelerated method for testing the corrodibility of metals and alloys in acid mine waters, which may be used in determining in the laboratory in a period of one or two days the relative tendency of metals and alloys to corrode in mine water, thus providing means for the mine operator to make more scientific selection of material, and means for the manufacturer to make quick tests on his products in the course of developing new acid-resisting alloys.

It is recognized that the test offered must be subjected to further study, and comparison made with actual practice, since no laboratory corrosion test can reproduce all the conditions prevailing in different mines. It is hoped that others will try this test, and report their experiences; meanwhile, further work along this line is also being carried out by the Bureau during the current year.

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William Cramp Sons Ship & Engine Building Co., The

ACCELERATED CORROSION TESTING OF METALS AND ALLOYS IN ACID MINE WATER.

By ROBERT J. ANDERSON, GEORGE M. ENOS, *and* J. RICHARD ADAMS.

INTRODUCTION.

The search for alloys that will withstand corrosive influences is one of the most energetically explored fields of physical metallurgy, but so far, experimenting has been on an empirical basis solely, and notably good results are quite accidental. In selecting metals and alloys for use as engineering materials of construction in structures where particularly corrosive atmospheres or solutions must be withstood, it is necessary to consider not only the physical properties of the materials but also their resistance to corrosion under the specific conditions of employment. The corrosion of alloys in acid mine water is a typical example of the failure of engineering materials from attack by corrosive solutions, and in selecting alloys for use in pumping equipment one of the most important properties for consideration is the corrodibility of the materials.

In the selection of alloys for withstanding corrosive conditions it is necessary that the selection be based on reliable and adequate tests, and so far, no standard method for corrosion testing has been developed. In determining the corrodibility of metals and alloys under specific conditions, two kinds of tests are normally carried out—namely, (1) laboratory or field tests, where the action of the corroding medium (liquid or gas) upon test samples of the material is examined; and (2), service tests, where the corrosion of parts in actual use is observed. Ordinarily, when the corrosion resistance of a metal or alloy in any liquid medium is to be determined, it is necessary to make actual immersion tests over a period of time. It is important to emphasize the fact that while long-time immersion tests are satisfactory from the point of view of the data secured thereby, they require too much time for completion; moreover, the results are not necessarily transferable into terms of service corrosion. Final results are definite in the service test, but much time is required, and the process of corrosion cannot be studied in detail in either test. There is no doubt of the demand that exists for an adequate accelerated test, but so far, no accelerated test has proved generally satisfactory, and no test that has been suggested yields results which can be translated into terms of service corrosion.

The corrosion of metals and alloys in specific corroding media like mineral acids, sea water, fresh waters, salt solutions, atmospheric air, and gases has been studied in detail for many years, but it is only recently that systematic investigation has been undertaken of the corrosion of materials in acid waters from coal mines. At the present time, the corrosion of pump parts (rods, valves, etc.) by such waters in the western Pennsylvania coal region is very serious; and it should also be added that corrosion of track, rolling stock, tools, and other equipment occurs when exposed to the action of acid waters.

In previous work by Selvig and one of the writers[1], investigation was made of the corrodibility of 45 metals and alloys on immersion in flowing acid waters of three coal mines of the western Pennsylvania region. It was shown that the following alloys had marked resistance to corrosion by the waters: (1) a high-chromium steel; (2) two chromium-nickel-silicon steels; (3) a high-silicon cast iron; and (4) a nickel-chromium-iron alloy. Investigation has been made by two of the writers[2] of the microscopic features of corrosion in the case of these 45 metals and alloys, also of the phenomenon of selective corrosion and the effect of grain size, while the coatings and films formed were examined.

Corrosion is generally regarded as a result of the tendency which a metal has for forming oxides or salts when in contact with a liquid or gaseous medium, and in the widest sense corrosion is the oxidation of a metal or alloy. During the many years that corrosion has been studied, various theories have been advanced to explain the mechanism of the phenomenon, and of all these, the electrolytic and direct oxidation theories are at present the most strongly supported.

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[1] Selvig, W. A., and Enos, G. M., Corrosion tests on metals and alloys in acid mine waters from coal mines: Bull. 4, Coal-Mining Investigations, Carnegie Inst. of Technology, Pittsburgh, 1922, 71 pp.

[2] Anderson, R. J., and Enos, G. M., Microstructural aspects of metals and alloys corroded by acid mine waters: Bull. 5, Coal-Mining Investigations, Carnegie Inst. of Technology, Pittsburgh, 1923, 44 pp.

OBJECT AND SCOPE OF INVESTIGATION.

The purpose of this investigation was to study the possibility of developing an accelerated test for determining the corrosion of metals and alloys in solution, particularly in acid mine water, and to correlate data obtained from such a test with data from long-time immersion tests.

Since corrosion has been regarded as being either chemical or electrolytic in character, according to the two principal schools of thought (although, in the opinion of the authors, there is no essential difference), an accelerated test might be developed which would be either chemical or electrolytic in nature. In either case, such tests are based on the assumption that corrosion is primarily a process of oxidation. This process may take place by direct reaction of a metal with oxygen or an oxidizing solution (chemical corrosion), or by electrolytic means. It is probable that chemical oxidation can be accelerated mechanically (by agitation), and by increasing the oxygen content of the solution. In so-called electrolytic corrosion, acceleration is obtained by both electrolytic and chemical means. While work was done during this investigation both on accelerated chemical and accelerated electrolytic testing, the latter offered more promise, and most of the results given are based on electrolytic tests.

In developing the accelerated electrolytic test, data obtained previously[8] in long-time immersion tests were correlated, and the correlation shows that the accelerated electrolytic test, as here developed, will be of considerable value for predicting service corrosion. Any accelerated test that will yield substantially the same results in a few hours as is obtainable only after several months, as in the long-time immersion test, obviously has great possibilities.

PREVIOUS WORK ON ACCELERATED CORROSION TESTING.

No accelerated test has so far been developed to a point where it will take the place of the long-time exposure tests which have been carried out in two ways—namely, (1) by observation tests made by users of materials; and (2), by systematic comparative tests made by investigators. Thus, in the case of the first mentioned, observations are continually being made by users of metals and alloys exposed to corrosive media, and replacements are made of parts for service based on general observation of the behavior and life of the materials. This test has the disadvantage that it requires considerable time before results are obtained. It should also be added that the initial installation may be expensive, and the results obtained will only hold for the conditions under which the test was carried out. In the case of systematic comparative tests made by investigators, samples of various metals and alloys are exposed to the corroding media, and data are taken for comparison as to the loss in weight, pitting, and other features over a period of time. Thus, the comparative long-time tests of Sabin[4] may be cited. He coated test pieces of aluminum, aluminum alloys and steel with various paints and varnishes, and suspended them in sea water for six months. They were then removed, and the loss in weight due to corrosion was measured.

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[8] Selvig, W. A., and Enos, G. M., work cited.

Chapman[5] has compared the "sulphuric-acid test," which has been widely used as an accelerated testing method, with long-time tests and shows that figures obtained by the sulphuric-acid test are of small value. This test consists essentially in submitting small polished specimens to the action of sulphuric acid (usually 20 per cent) for a definite time period (usually 1 hour). The pieces are carefully weighed before immersion, and after removal are cleaned, dried, and weighed. The loss in weight is taken as a measure of the resistance of the material to corrosive influences.

The practice of making corrosion tests by simply immersing small specimens of the material in vessels containing sulphuric acid, or other corroding media, either exposed to the air, or sealed, has been common practice for many years. Attempts to improve upon this have been made and reported in the literature, but these are so numerous that only a few need be cited. Thus, Aupperle and Strickland[6] immersed test pieces of iron and steel in sulphuric acid in tanks, caused circulation and aeration of the solution by means of an air-lift, and maintained the acidity of the solution as nearly constant as possible by frequent analysis and addition of acid as needed. A method has been developed by the U. S. Bureau of Standards for making accelerated tests wherein the pieces are alternately immersed in the liquid and exposed to the air.

Acceleration of the corrosion rate by imposing a current upon the metal to be tested, making it anode in the corroding electrolyte, has been tried by several investigators. Whipple and Whipple[7] used the electric current to accelerate the corrosion rate in various tests, and found that accelerated electrolytic tests made in running water indicate the manner in which the material (steel) will fail in service, though not necessarily the rate. Hanson and Lewis[8] studied the effect of one metal upon another by connecting electrodes of the two metals through an ammeter, the electrolyte being the corroding medium. In these tests, quantitative measurement of the corrosion rate was not made. Byers and Voris[9], in studying the corrosion loss of iron in the passive state under boiler conditions, used an accelerated electrolytic test—that is, they imposed a current upon the iron in a cell, the iron being anode. The voltage and current were carefully measured and the losses noted.

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[4] Sabin, A. H., The industrial and artistic technology of paint and varnish, New York, 1905, John Wiley & Sons, pp. 220-240.

[5] Chapman, C. M., Value of the sulphuric acid test: Proc. Amer. Soc. for Test. Mat., vol. 11, 1911, pp. 609-614.

[6] Aupperle, J. A., and Strickland, D. M., Observations on the corrosion of iron and steel: Trans. Amer. Electrochem. Soc., vol. 39, 1921, pp. 123-133.

Desch and his collaborators[10] have corroded small pieces of brasses in sea water by means of an imposed electric current, the specimen being anode in a small cell, and the cathode being platinum, the purpose of the investigation being to study the microscopy of corrosion. They concluded that there is no real difference between natural corrosion in sea water and the corrosion accelerated by means of the electric current.

The most promising method of accelerated testing, and the one on which a great deal of the present work is based, is the anodic corrosion test. In this, the piece to be tested is made anode in a cell containing the corroding medium as electrolyte, while a platinum wire is used as cathode. A very small current is passed through this cell, and the corrosion losses are determined for any given length of time. Curry[11] used this method to determine corrosion losses of copper-tin alloys in various electrolytes, and the same method was applied in investigation of the corrosion of copper-zinc alloys by Lincoln and his co-workers[12]. These investigations were however, of little value in the formulation of an accelerated test. Rowland[13] ran similar experiments on copper-aluminum alloys. This matter seems to have been forgotten until recent years when Brown and his co-workers[14] determined the effect of current density, temperature, and concentration of the corroding medium (sodium hydroxide) on corrosion losses. Feuer[15] has described various methods of corrosion testing, including a method of measuring the fall of potential between the surface of the metal and the solution, using an auxiliary electrode. The current is measured, and the plotted current-potential curve, gives an indication of the corrosion rate in the electrolyte. Using the same or a similar method, Reedy and Feuer[16] have studied the corrosive influence of the ions in natural waters and other factors affecting corrosion rates. Belladen[17] has made a large number of electrolytic tests on 70:30 brass, and claims that this is a good method to study corrosion. He does admit, however, that the results are not always similar to practical results, because the protective action of the film of salts, which the prolonged action of the current destroys, may be absent.

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[7] Whipple, G. C., and Whipple, M. C., Mill scale as a cause of the pitting of steel pipes: Proc. 8th Intern. Cong. App. Chem., vol. 21, 1912, pp. 155-183.

[8] Hanson, H. H., and Lewis, W. K., Method for testing the mutual corrosive effect of metals: Trans. Amer. Electrochem. Soc., vol. 22, 1912, pp. 259-261.

[9] Byers, H. G., and Voris, F. T., Passivity of iron under boiler conditions: *Jour.* Amer. Chem. Soc., vol. 34, 1912, pp. 1368-1379.

[10] Desch, C. H., and Whyte, S., The micro-chemistry of corrosion: Part I—Some copper-zinc alloys: *Jour.* Inst. of Metals, vol. 10, 1913, pp. 304-323.

Whyte, S., and Desch, C. H., The micro-chemistry of corrosion: Part II—The alpha-alloys of copper and zinc: *Jour.* Inst. of Metals, vol. 11, 1914, pp. 235-245.

Whyte, S., The micro-chemistry of corrosion: Part III—The alpha-beta alloys of copper and zinc: *Jour.* Inst. of Metals, vol. 13, 1915, pp. 80-90.

Desch, C. H., and Hyman, H., The micro-chemistry of corrosion: Part IV—Gun-metal: *Jour.* Inst. of Metals, vol. 14, 1915, pp. 189-197.

[11] Curry, B. E., Electrolytic corrosion of the bronzes: *Jour. Phys. Chem.*, vol. 10, 1906, pp. 474-499.

As a result of studying the corrosion of easily corrodible alloys of aluminum, Rolla and his co-workers[18] claim that the corrosion of all alloys is not necessarily an electro-chemical process, and in zinc-aluminum alloys it is a chemical process.

Harder and McFarland[19] have published a valuable paper on various factors entering into the corrodibility of metals. One interesting conclusion put forth in their paper is that the relative amounts of corrosion can not be predicted from relative electromotive forces.

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[12] Lincoln, A. T., Klein, D., and Howe, P. E., Electrolytic corrosion of brasses: *Jour. Phys. Chem.*, vol. 11, 1907, pp. 501-536.

Lincoln, A. T., and Bartells, Jr., G. C., Electrolytic corrosion of brasses in synthetic sea water: *Jour. Phys. Chem.*, vol. 12, 1908, pp. 550-556.

[13] Rowland, W. S., The electrolytic corrosion of the copper-aluminum alloys: *Jour. Phys. Chem.*, vol. 12, 1908, pp. 180-206.

[14] Brown, O. W., Henke, C. O., and Smith, L. T., Anode corrosion of lead in sodium hydroxide solutions: *Jour. Phys. Chem.*, vol. 24, 1920, pp. 367-378.

[15] Feuer, B., Tests for relative corrosion: *Chem. and Met. Eng.*, vol. 22, 1920, pp. 1197-1198.

[16] Reedy, J. H., and Feuer, B., The corrosion of brass in dilute electrolytes: *Jour. Ind. and Eng. Chem.*, vol. 12, 1920, pp. 541-547.

[17] Belladen, I. L., The corrosion of some complex brasses in sea water: *Gazz. Chim. Ital.*, vol. 51, 1921, pp. 144-159; Abstd. in *Chem. Absts.*, vol. 16, 1922, pp. 893-894.

[18] Rolla, L., Frassinati, M., and Bulli, M., The corrosion of some alloys of aluminum: *Gazz. Chim. Ital.*, vol. 52, 1922, pp. 79-87; Abstd. in *Chem. Absts.*, vol. 16, 1922, p. 1732.

[19] Harder, O. E., and McFarland, D. F., Preliminary study of alloys of chromium, copper, and nickel: Univ. of Ill. Eng. Exp. Sta. Bull. 93, 1916, pp. 20-23.

The electrolytic theory has been made use of considerably in explaining many cases of corrosion—for example, the corrosive effect of current leakage from electric railways on nearby buried pipes. Considerable work has been done on this subject by McCollum and his co-workers[20] at the laboratory of the U. S. Bureau of Standards. These workers, as well as many others, have shown that the corrosion of iron in reinforced concrete is also explained by the electrolytic theory.

The electrolytic theory of corrosion has also found application in various methods for protecting boilers and structures against corrosion. Cumberland[21] has attacked the problem of the protection of boilers from this point of view. In a process developed by him, pieces of iron are suspended in the water, and are connected with a low-tension dynamo generating continuous current. This method is found to work well, and the hydrogen liberated even tends to loosen the boiler scale. It has also been found that iron can be protected by means of copper-zinc alloys. Jorissen[22] demonstrates that copper-zinc alloys containing less than 35 per cent copper will protect iron when in contact with it, and those with more than 35 per cent copper will act just oppositely.

It is also known that if one metal is coated with another, corrosion may be inhibited; but care must be taken to ensure a perfectly uniform coating. Thus, if iron is coated with zinc, the iron is protected as long as the zinc coating is perfect. As soon as this is broken, a small galvanic cell is set up, and the corrosion of the iron is greatly accelerated. A good example of galvanic action has been noted by Landis[23]. He found that after the gold wore off the points of some gold-coated steel pens, the corrosive action was exceedingly rapid, the pen being useless after two days. He explains this by showing that there is a steel/ink/gold galvanic cell set up.

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[20] McCollum, B., and Logan, K. H., Electrolytic corrosion of iron in soils: Tech. Paper 25, Bureau of Standards, June 12, 1913; and other papers.

[21] Cumberland, E., Electrolytic method of preventing corrosion: *Water and Water Eng.*, vol. 18, 1916, pp. 86-90.

[22] Jorissen, W. P., "Galvanic" protection of iron in water by means of copper-zinc alloys: *Chem. Weekblad*, vol. 13, 1916, pp. 1020-1025; Abstd. in *Chem. Absts.*, vol. 10, 1916, p. 3057.

[23] Landis, W. S., The electrolytic corrosion of electroplated objects: Trans. Amer. Electrochem. Soc., vol. 19, 1911, pp. 59-67.

Bancroft[24] has discussed accelerated corrosion tests for metals and alloys, indicating that the most suitable test when properly developed will probably be an electro-chemical one.

EXPERIMENTAL WORK ON THE DEVELOPMENT OF AN ACCELERATED TEST.

Review of the literature on corrosion, and particularly on accelerated corrosion testing, has shown that no method of testing so far developed can supplant the long-time test and actual experience in judging the resistance to corrosion of metals and alloys, particularly in a corrosive medium such as acid mine water. Since a real need does exist for an accelerated test, which in a few hours will give results comparable to long-time tests, and when properly correlated with microscopic observations and known physical characteristics will give a measure of the probable life of the material under service conditions, experiments were carried out with the object of determining whether a method could be developed.

It has been pointed out previously that the two most strongly supported corrosion theories at the present time are those of electrolytic action and simple (or direct) oxidation. The position has been recently taken by some investigators, notably Bengough and Stuart[25], that corrosion may be either chemical or electro-chemical in nature; these investigators prefer the term "electro-chemical corrosion" to "electrolytic corrosion," and they distinguish between chemical and electro-chemical corrosion as follows:

> Chemical reactions are characterized by the liberation of a portion of the energy of the system in the form of heat; and by the necessity of contact between the reacting bodies. The reacting substances may be either molecular or ionic.
>
> Electro-chemical reactions are characterized by the liberation of a portion of the energy of the system as electrical energy, and by the condition that the reacting substances must be capable of ionization, and must be spatially separated. They must, however, be connected by two conducting paths, one an electrolyte, and the other a metallic conductor. At one of the metal electrolyte junctions, called the anode, oxidizing reactions take place; at the other, called cathode, corresponding reducing actions. Consequently all electro-chemical corrosion must take place at the anode.

The experimental work carried out by the authors of this Bulletin developed logically in two directions—namely, (1) development of an accelerated chemical test; and (2), development of an accelerated electrolytic test.

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[24] Bancroft, W. D., Preliminary notes on corrosion: Proc. Am. Soc. Test. Mat., vol. 22, 1922, pp. 232-236.

[25] Bengough, G. D., and Stuart, J. M., The nature of corrosion and the function of colloids in corrosion, with an appendix on terms used in colloid chemistry. Sixth report to the Corrosion Research Committee of the Institute of Metals: *Jour.* Inst. of Metals, vol. 28, 1922, pp. 31-114.

CHEMICAL TEST.

The attempt was first made to develop an accelerated chemical test, but the results were negative. Bancroft suggests[26] that since oxygen acts as a depolarizer, results qualitatively comparable to those obtained in long-time immersion tests should be obtained by a chemical test in which air or oxygen is bubbled through the corroding medium. The authors' first attempt to develop an accelerated corrosion test was to maintain oxygen in contact with the metal immersed, by bubbling air through the corroding medium.

This chemical test was carried out on 12 selected metals and alloys of the same composition as some of those which were used for long-time immersion tests in a previous investigation[27]. The compositions of these materials are given in Table 1, which also gives the results obtained. The corroding medium was acid water from the Edna No. 2 mine of the Hillman Coal & Coke Co., at Wendel, Westmoreland County, Pa., and the free acidity was 2,020 parts per million, in terms of sulphuric acid. The total acidity of this water, due to free sulphuric acid plus sulphates of iron and aluminum, was about 12,000 p.p.m. Certain of the materials tested were in the cast condition, while others were in the form of rolled sheet, and the tests were carried out as follows:

The pieces were cut in the form of parallelopipeds of such dimensions as to give a total area of from 3 to 4 square inches. Thus, in the case of the cast materials, the dimensions were ¼ inch by ¼ inch by 3 inches while with the rolled pieces they were ½ inch by ⅛ inch by 3 inches. These pieces were attached to a glass rod by a piece of twine, and this rod was then laid across the lip of a 150-c.c. bottle, by which means the test pieces were suspended and did not come in contact with any portion of the glass. The liquid in which the piece was to be tested was placed in the bottle, enough being added to cover an area of 1.75 square inches. Air was then bubbled through the solution, the stream of air coming into such intimate contact with the piece as the set-up permitted.

It was found necessary to replenish the water every other day, as the oxygen of the air caused the iron to precipitate. Twelve alloys were tested under the above conditions for 30 days. After this the pieces were removed, the coatings were brushed off the corroded pieces while in a stream of water, and the pieces were dried and weighed. Table 1 gives the data obtained in these experiments, and comparison is drawn between the losses so obtained and those obtained in the long-time exposure tests of the previous investigation[28].

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[26] Private communication, Sept., 1922.

[27] Selvig, W. A., and Enos, G. M., work cited.

In Figure 1 the losses obtained in the long-time immersion and the chemical tests are compared graphically. · From the graphs it is at once apparent that the losses show no similarity in their relative order. The divergence between the two graphs shows plainly that an approximate factor cannot be applied for translating the results of the chemical corrosion into terms of long-time corrosion. It should also be pointed out that the loss per day is much too small, and this means that it would require too long a time to complete such a test. From the graphs it is evident that this so-called accelerated test is two to three times slower than the long-time immersion test. This may be due to the fact that air was

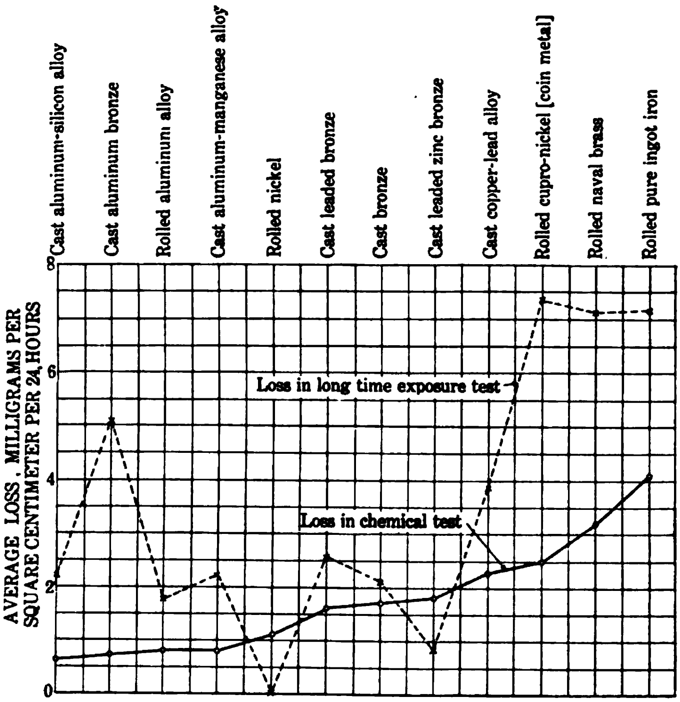

FIGURE 1.—*Comparison of corrosion losses in chemical test with losses in long-time exposure test.*

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[28] Selvig, W. A., and Enos, G. M., work cited.

TABLE 1.—*Comparative loss in weight of test pieces in chemical corrosion test, and in long-time immersion test, in Edna No. 2 mine water.*

Test piece number.[a]	Designation.	Chemical composition, per cent.[b]	Area of test pieces, sq. cm.	Weight in grams.		Loss in weight, grams.	Loss per sq. cm. per 24 hours, in accelerated test, milligrams.	Loss per sq. cm. per 24 hours, in long-time exposure test,[d] milligrams.
				Before immersion.	After immersion.			
22	Rolled naval brass	[c] Cu 60.40 Zn 38.83 Sn 0.77	11.3	6.2801	5.1916	1.0885	3.2	....
23			11.3	6.1702	5.1082	1.0620	3.1	....
Average			....	....	....	....	3.2	7.11
37	Rolled cupro-nickel (coin metal)	Cu 74.60 Ni 25.40	11.3	7.9908	7.1105	0.8803	2.6	....
38			11.3	8.0996	7.2630	0.8366	2.5	....
Average			....	....	....	....	2.5	7.34
70	Cast copper-lead alloy	Cu 53.40 Pb 46.4	11.3	64.7889	64.0082	0.7807	2.3	....
71			11.3	69.0517	68.2930	0.7587	2.2	....
Average			....	....	....	....	2.3	3.87
73	Cast lead-zinc bronze	Cu 86.34 Pb 0.83 Sn 11.24 Zn 1.60	11.3	44.7944	44.2510	0.5434	1.6	....
74			11.3	42.4359	41.7198	0.7161	2.1	....
Average			....	....	....	....	1.8	0.83
76	Cast aluminum bronze	Cu 93.9 Al 6.1	11.3	29.9203	29.6894	0.2309	0.7	....
77			11.3	31.6555	31.3941	0.2614	0.8	....
Average			....	....	....	....	0.7	5.08
79	Cast bronze	Cu 89.8 Sn 9.7 Pb 0.5	11.3	42.2925	41.7456	0.5469	1.6	....
80			11.3	35.0612	34.4503	0.6109	1.8	....
Average			....	....	....	....	1.7	2.12
82	Cast lead-bronze	Cu 87.5 Sn 10.6 Pb 1.6	11.3	42.7461	42.2449	0.5012	1.5	....
83			11.3	39.3069	38.7085	0.5984	1.8	....
Average			....	....	....	....	1.6	2.56
88	Cast aluminum-silicon alloy	Si 3.9 Al 96.1 (by difference)	11.3	10.4028	10.1960	0.2068	0.6	....
89			11.3	10.4830	10.2951	0.1879	0.6	....
Average			....	....	....	....	0.6	2.20
91	Cast aluminum-manganese alloy	Mn 1.81 Al 98.19 (by difference)	11.3	12.4203	12.1766	0.2437	0.7	....
92			11.3	11.8851	11.6039	0.2812	0.8	....
Average			....	....	....	....	0.8	2.23
97	Rolled aluminum alloy	Cu 3.62 Si 0.56 Mn 0.46 Fe 0.45 Al 94.91 (by difference)	11.3	2.4792	2.1991	0.2801	0.8	....
98			11.3	2.4075	2.1220	0.2855	0.8	....
Average			....	....	....	....	0.8	1.76
115	Rolled ingot iron	[c] Fe 99.9	11.3	6.3639	4.9509	1.4130	4.2	....
116			11.3	5.9848	4.6455	1.3393	3.9	....
Average			....	....	....	....	4.1	7.14
121	Rolled nickel	[c] Ni 99+	11.3	7.3667	6.9839	0.3828	1.1	....
122			11.3	5.6114	5.2175	0.3939	1.1	....
Average			....	....	....	....	1.1	0.003

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[a] *Test piece numbers used are the same as those used in Bulletins 4 and 5, Coal-Mining Investigations, Carnegie Inst. of Technology, 1922-1923.*

[b] *Analyses, unless otherwise noted, were made by C. H. Eldridge and G. B. Dalrymple.*

[c] *Analysis furnished by co-operating company.*

[d] *Average figures from Bull. 4, Coal-Mining Investigations, Carnegie Inst. of Technology, 1922.*

bubbled through the solution for only about 8 hours a day. Apparently, this test tends to duplicate the long-time immersion test. The great variability of the results is probably due to a number of factors, some of which could only be regulated with difficulty. These factors are as follows:

1. The speed of bubbling air through the solution. While this can be governed more or less closely, the regulation was poor in the tests made due to variations in the source of the air at different times.

2. The tendency for the liquid to spatter on the piece. This causes corrosion above the surface of the liquid, but could probably be stopped by coating the upper portion of the test piece with some material such as paraffin.

3. Deposition of salts and metals—for example, iron salts from the water—on the test pieces. This would cause trouble due to the fact that small galvanic cells would be set up. Off-hand this might seem to be a favorable condition, but the difficulty is that the amount of material adhering varies between wide limits, and this results in setting up a variable number of cells, thus causing more or less galvanic action depending on the adhering layer. At present there seems no way to prevent this.

4. A strongly adsorbed layer of liquid acting as a coating to the piece. If such an adsorbed layer exists, then the active oxygen will comprise only a small amount of the available oxygen, being only that oxygen which is in the adsorbed layer of liquid. This might be overcome by increasing the rate of bubbing the oxygen; but it appears improbable that the oxygen would pass through fast enough to wash off this layer.

5. Hydrolysis of the mine water. This was found to take place in a very short time. In such solutions as mine water this would cause considerable trouble as the solution would have to be changed constantly.

It is therefore concluded that, as an accelerated test, the chemical method just described seems to be of little value in dealing with mine water corrosion. However, the surface appearances of the samples exposed to the accelerated chemical test were very similar to that of those exposed to the long-time test. On this basis it appears that there is a possibility that the test might yield comparative results in the corrosion of metals and alloys in solutions containing no heavy metals.

Table 2 gives a tabulated description of the coatings obtained on each metal and alloy; in general, the coatings were similar. For the materials where there was no agreement, it seems evident, with one exception, that a similar condition would result if the pieces had been left in the chemical test for a longer time. In the one exception, rolled cupro-nickel, it appeared that the corrosion process had been allowed to proceed much too far in the accelerated chemical test.

TABLE 2.—*Comparison of the surface appearance of test pieces from the chemical test and the long-time immersion test.*

Test piece number.[a]	Designation.	Surface appearance of test pieces from the chemical test.	Surface appearance of test pieces from the long-time immersion test.
22, 23	Rolled naval brass	Bright crystalline surface	Covered with a coating of copper; bright surface below coating.
37, 38	Rolled cupro-nickel	Corroded a little more, giving a slightly roughened surface	Slightly tarnished.
70, 71	Cast copper-lead alloy	Only traces of characteristic coating	Covered with a soft grey coating.
73, 74	Cast lead-zinc bronze	Identical	Soft, bluish grey coating.
76, 77	Cast aluminum bronze	Coated with copper	Totally corroded to copper.
79, 80	Cast bronze	Identical	Covered with a bluish grey coating.
82, 83	Cast lead-bronze	Identical	Covered with an uneven greenish-blue coating.
88, 89	Cast aluminum-silicon alloy	Pitted, with the same general appearance	Badly pitted, with a spongy lead appearance.
91, 92	Cast aluminum-manganese alloy	Same characteristic pitting	Badly pitted, but had a bright appearance.
97, 98	Rolled aluminum alloy	Very similar	Badly pitted.
115, 116	Rolled ingot iron	Same appearance	Covered with a red rust and pitted.
121, 122	Rolled nickel	Practically the same	Slightly tarnished with little loss in weight.

[a] *Test piece numbers used are the same as those in Bulletins 4 and 5, Coal-Mining Investigations, Carnegie Inst. of Technology, 1922-1923.*

While the method of accelerating the chemical corrosion test by bubbling air through the corroding medium did not meet with much success in the case of mine water tests, in other media, such as sodium chloride or sulphuric acid, may possibly be of value. It may also be possible to use some corroding media that will oxidize the metal to be tested much faster (and in direct proportion) than the corroding media in which the metal is to be used in service. It should also be pointed out that the set-up in this test may be improved so as to secure better contact of the oxygen or air with the test sample.

ACCELERATED ELECTROLYTIC TEST.

Since previous work, particularly by Curry, Lincoln, Rowland, and others, on the electrolytic corosion of alloys had indicated that there were good possibilities for developing an accelerated electrolytic test, the previous work of Curry[29] was repeated in part in order to ascertain whether duplicate results could be obtained.

DESCRIPTION OF TESTS.

During the repetition of Curry's work, which was carried out by the authors, electrolytic corrosion tests were first made on copper-tin alloys of the following nominal compositions: 88:12; 67:33; 30:70; and 11:89 Cu-Sn. The alloys were prepared in the laboratory from high-grade primary copper and tin, and the necessary precautions were observed to ensure proper condition of the samples for testing. Test pieces were poured of cylindrical shape 0.8 cm. in diameter and 8.0 cm. long, and these were annealed in order to normalize the alloys. Anodic corrosion tests were made on these alloys in four different electrolytes, using platinum wire as the cathode. The electrolytes, employed at room temperature, were the following: 6.5 per cent sodium chloride by weight in aqueous solution; 6.5 per cent sodium sulphate; 6.5 per cent sodium nitrate; and 3 per cent ammonium oxalate plus 3 per cent oxalic acid by weight in aqueous solution. The tests were carried out on a standard Braun electrolytic cabinet, such as is used for the electrolytic analysis of metals and alloys. The area of test piece exposed was 14 sq. cm. The cylindrical test pieces were attached to the revolving spindles of the electrolytic apparatus by means of heavy copper wire soldered to each piece, and the speed of rotation was maintained constant at 140 r.p.m. The current was regulated to give a current density of 0.179 amp. per sq. dcm. of surface exposed, and the test period was 8 hours. Heavy walled glass beakers were employed for the cells, and about 300 c.c. of electrolyte was used in each run.

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[29] Curry, B. E., work cited.

Table 3 gives the actual corrosion losses obtained by the authors compared with the corresponding results of Curry. It was necessary to interpolate Curry's data because of variation in the composition of the alloys. Table 4 has been calculated from Table 3 on the basis of the gram-weight loss per sq. cm. per 24 hours with a calculatd current density of 10 amps. per sq. dcm., and this gives more convenient figures for comparison. The formula employed for calculating was,

$$\frac{\dfrac{\text{Total gram weight loss x time-factor}}{\text{Area exposed (in sq. cm.)}}}{\dfrac{\text{Amperage}}{\text{Area exposed (sq. dcm.)}}} \times 10$$

Tables 3 and 4, on comparative electrolytic corrosion losses of four copper-tin alloys, follow:

TABLE 3.—*Comparative electrolytic corrosion losses of four copper-tin alloys in four electrolytes (current density 0.179 amp. per sq. dcm.; 8-hour runs) as obtained by the authors and by Curry (see Table 4).*

Nominal composition of the alloys,[a] elements per cent.		Electrolyte; 6.5 per cent sodium sulphate solution.		Electrolyte; 6.5 per cent sodium chloride solution.		Electrolyte; 6.5 per cent sodium nitrate solution.		Electrolyte; 3 per cent ammonium oxalate plus 3 per cent oxalic acid.	
		Total weight loss, grams.		Total weight loss, grams.		Total weight loss, grams.		Total weight loss, grams.	
Cu	Sn	Authors.	Curry.	Authors.	Curry.	Authors.	Curry.	Authors.	Curry.
88	12	1.91[b]	0.33	2.95[b]	....	1.94[b]	0.26	0.26[b]	0.24
67	33	0.03	0.005	0.24	0.11	0.24	0.02	0.27	0.24
30	70	0.01	0.10	0.29	0.15	0.04	0.25	0.25	0.20
11	89	0.19	0.30	0.20	0.14	0.99	1.20	0.66	0.53

[a] *Area exposed—Authors, 14 sq. cm.; Curry, 13.8 sq. cm.*

[b] *These figures were obtained with current density of 1.79 amps. per sq. dcm.*

TABLE 4.—*Comparative electrolytic corrosion losses per unit area for four copper-tin alloys in four electrolytes (current density calculated to 10 amps. per sq. dcm.) (See Table 3.)*

Nominal composition of the alloys, elements per cent.		Electrolyte; 6.5 per cent sodium sulphate solution.		Electrolyte; 6.5 per cent sodium chloride solution.		Electrolyte; 6.5 per cent sodium nitrate solution.		Electrolyte; 3 per cent ammonium oxalate plus 3 per cent oxalic acid.	
		Weight loss per sq. cm. per 24 hrs., grams.		Weight loss per sq. cm. per 24 hrs., grams.		Weight loss per sq. cm. per 24 hrs., grams.		Weight loss per sq. cm. per 24 hrs., grams.	
Cu	Sn	Authors.	Curry.	Authors.	Curry.	Authors.	Curry.	Authors.	Curry.
88	12	2.29	3.96	3.54	....	2.32	3.12	0.31	2.82
67	33	0.36	0.06	2.86	1.32	2.84	0.24	3.27	2.88
30	70	0.12	1.20	3.45	1.00	0.48	5.00	2.98	2.40
11	89	2.31	3.60	2.38	1.68	11.87	14.4	7.92	6.86

Using the data in Table 4, the graphs of Figure 2 were drawn, plotting the loss in weight against the copper content of the alloys, and these graphs show that there is good general agreement between the authors' results and those of Curry. It should be pointed out that in the authors' tests the corroded test pieces were not reduced in hydrogen as in Curry's work, and this may account in part for discrepancies in the results. It is true that while there is good general agreement among the figures there is not exact agreement. This is due to several factors; the speed of rotation employed by the authors and by Curry was probably not the same; and the nominal compositions of the alloys are different in all cases; moreover, Curry's data were interpolated in order to obtain comparison. However, the graphs in Figure 2 show that good relative agreement is obtained. The results of these tests and

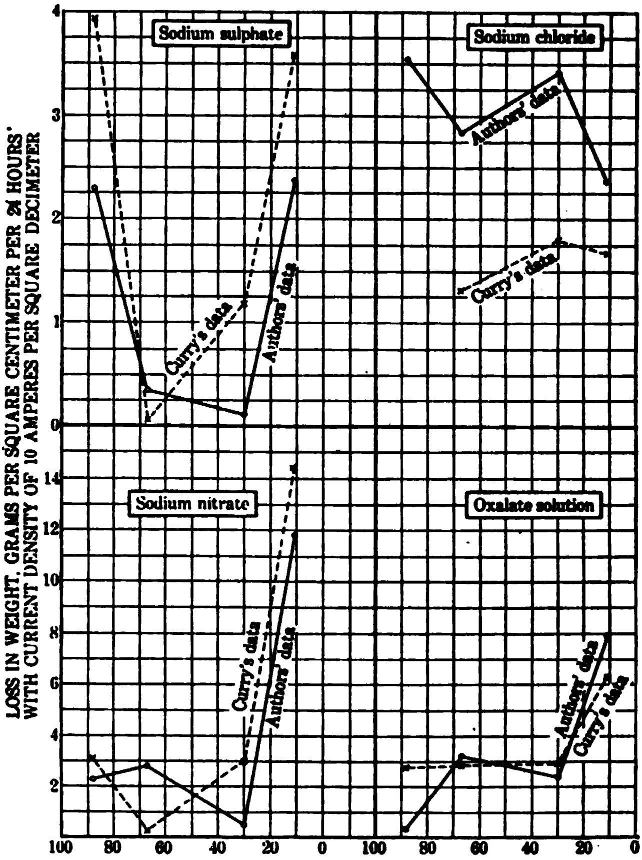

FIGURE 2.—*Comparison of corrosion loss and composition of copper-tin alloys in different solutions as obtained by the authors and Curry.*

others indicated that Curry's method of experiment could be accepted as a basis for further investigation in devising an accelerated test for corrosion.

FACTORS AFFECTING LOSS IN WEIGHT BY ACCELERATED ELECTROLYTIC CORROSION.

Having shown that it was readily practicable to obtain results in agreement with previous work by the electrolytic method, experiments were next made to determine the effects of several factors on the loss in weight by anodic corrosion. There are a number of factors which affect results in accelerated electrolytic corrosion testing, but certain of these are of minor importance, and may properly be neglected for practical purposes. The factors affecting any corrosion process are numerous, but these can not be discussed even in a general way in this bulletin. Given a specific alloy and a specific electrolyte, the factors which are of greatest importance in affecting corrosion rates in the accelerated electrolytic test include the following: variation in (1) current density, (2) time of exposure, (3) temperature, and (4) speed of rotation. A set of experiments was made to determine the effects of these variables upon corrosion rates, but unfortunately all of these had not been completed up to the time of publication. The results obtained in the completed experiments, however, are given below.

CURRENT DENSITY.

Some tests were made on the accelerated electrolytic corrosion of 90:10 and 70:30 Cu-Sn alloys, using 6.5 per cent sodium nitrate as the electrolyte, with the current density varied over the range 0.179 to 2.64 amps. per sq. dcm. These tests were carried out in the same way as in the case of the four copper-tin alloys discussed above, and the results are given in Table 5. In these runs the amperage was maintained constant, and the current density was varied by varying the amount of the submerged areas of the test pieces. In passing, it is perhaps quite unnecessary to state that the weight loss is not necessarily proportional to the quantity of electricity imposed—that is, to the amperage. It is evident that since the current density is the result of amperage divided by the area from which the current passes, variation of either amperage or immersed area will produce variation in current density. Hence, in testing, the amperage or immersed area may be varied, as is most convenient, in order to vary the current density.

Additional runs were made using a number of different metals and alloys in given electrolytes, and a typical industrial alloy (naval brass) in several electrolytes, and varying the current density over the aproximate range 0.125 to 5.8 amps. per sq. dcm. For these tests, the following metals and alloys were corroded in dilute sulphuric acid (15,760 p.p.m.); 90:10 and 65:35 Cu-Sn alloys; various brasses, including a high brass (67:33 Cu-Zn), a low brass (80:20 Cu-Zn), a naval brass (60:39:1 Cu-Zn-Sn), and admiralty metal (70:29:1 Cu-Zn-Sn); and copper, and iron. The copper-tin alloys were in cast form, and the other materials in sheet form. Naval brass sheet (60:39:1 Cu-Zn-Sn) was also corroded in the following solutions: Edna No. 2 mine water (free acidity 2,020 p.p.m.): dilute sulphuric acid (15,760 p.p.m.); sea water, 4 per cent sodium chloride; sodium-chloride solution, 8 per cent NaCl; and sodium-hydroxide solution, 1 per cent NaOH.

TABLE 5.—*Effect of variation in current density on loss in weight (amperage constant) for two alloys, in 6.5 per cent sodium-nitrate solution; duration of run, 8 hours.*

Area submerged, sq. cm.	Current density, amperes per sq. dcm.	Total loss in weight, grams.		Loss in weight per sq. dcm., grams.		Loss in weight per sq. dcm., for unit current density, grams.	
		90:10 Cu-Sn alloy.	70:30 Cu-Sn alloy.	90:10 Cu-Sn alloy.	70:30 Cu-Sn alloy.	90:10 Cu-Sn alloy.	70:30 Cu-Sn alloy.
13.96	0.179	0.2088	0.2302	1.49	1.64	8.3	9.2
8.19	0.305	0.2326	0.2717	2.84	3.32	9.3	10.9
4.95	0.505	0.2279	0.1046	4.60	2.11	9.1	4.2
3.55	0.704	0.2458	0.1130	6.93	3.18	9.8	4.5
7.99	0.876	0.7492	0.2126	9.37	2.66	10.7	3.0
5.25	1.33	0.7164	0.1502	13.6	2.86	10.2	2.2
3.99	1.75	0.7112	0.1517	17.8	3.80	10.2	2.2
2.65	2.64	0.6228	0.2458	23.5	9.28	8.3	3.5

In these runs, the immersed areas of the test pieces were maintained as constant as possible, and the current density was varied by varying the amperage. The results of these tests are given in Tables 6 and 7 and the data from Tables 5 and 6 are plotted in the graphs of Figure 3, and those from Table 7 in Figure 4. In Figure 3 the data for the different brasses (including copper) are plotted on one curve (designated *5*, Brass), because the weight losses are so close together that separate curves are unnecessary. Also in Figure 3, the 90:10 Cu-Sn alloy (designated *1*, 90:10 Cu-Sn alloy), and the 70:30 Cu-Sn alloy (designated *3*, 70:30 Cu-Sn alloy) were corroded in 6.5 per cent sodium-nitrate solution; and the other materials were corroded in dilute sulphuric acid.

TABLE 6.—*Effect of variation in current density upon the corrosion rate of some metals and alloys in dilute sulphuric acid; duration of run, 4 hours.*

Test piece number.	Immersed area, sq. cm.	Total loss in weight, grams.	Current, amperes.	Current density, amperes per sq. dcm.	Loss in mg. per sq. cm. per 24 hours.	Voltage drop, per cell.
High brass—Cu 66.55, Zn 33.45.						
16-1	14.26	0.1053	0.020	0.140	44	1.0
16-2	14.52	0.1952	0.040	0.278	81	1.5
16-3	14.04	0.2661	0.070	0.469	107	1.0
16-4	14.91	0.5055	0.110	0.740	203	1.5
16-5	14.40	0.7387	0.155	1.078	308	1.0
16-6	14.51	1.1713	0.260	1.796	485	1.8
16-7	14.00	2.3394	0.470	3.357	1003	2.4
16-8	14.36	4.0130	0.810	5.640	1672	4.7
Low brass—Cu 80.09, Zn 19.91.						
19-1	14.71	0.1037	0.020	0.136	43	1.0
19-2	14.44	0.1922	0.040	0.276	80	1.0
19-3	14.97	0.3324	0.070	0.467	133	1.0
19-4	14.82	0.5069	0.110	0.742	205	1.0
19-5	13.93	0.7388	0.155	1.112	318	1.0
19-6	14.62	1.1645	0.260	1.770	480	1.7
19-7	14.06	2.3295	0.470	3.357	994	2.3
19-8	15.04	3.9903	0.810	5.420	1602	4.3
Naval brass—Cu 60.04, Zn 38.83, Sn 0.77.						
22-1	14.49	0.1040	0.020	0.138	43	1.0
22-2	14.57	0.1932	0.040	0.275	80	1.0
22-3	14.43	0.3312	0.070	0.485	138	1.0
22-4	14.95	0.5167	0.110	0.736	208	1.0
22-5	13.86	0.7584	0.155	1.124	330	1.0
22-6	14.77	1.2269	0.260	1.760	498	1.85
22-7	14.06	2.4848	0.490	3.500	1060	3.0
22-8	13.96	4.1610	0.810	5.800	1788	4.3
Copper.						
25-1	14.15	0.1098	0.020	0.141	47	1.0
25-2	13.89	0.1986	0.040	0.288	86	1.0
25-3	15.81	0.3376	0.070	0.440	128	1.0
25-4	14.79	0.5405	0.110	0.745	220	1.0
25-5	14.30	0.7423	0.155	1.080	311	1.0
25-6	14.06	1.1799	0.260	1.850	503	1.8
25-7	14.44	2.3294	0.470	3.250	968	2.2
25-8	13.94	3.9889	0.810	5.810	1717	5.0
Admiralty metal—Cu 70.80, Zn 28.06, Sn 1.14.						
28-1	14.67	0.1035	0.020	0.136	42	1.0
28-2	13.86	0.1898	0.040	0.289	82	1.0
28-3	13.81	0.3284	0.070	0.506	143	1.0
28-4	14.64	0.5050	0.110	0.751	207	1.0
28-5	14.00	0.7376	0.155	1.107	316	1.0
28-6	13.96	1.1808	0.260	1.860	507	2.1
28-7	14.35	2.3904	0.500	3.480	999	2.7
28-8	14.43	4.0654	0.810	5.600	1690	5.0
Iron.						
115-1	13.93	0.0975	0.020	0.143	42	1.0
115-2	15.35	0.1783	0.030	0.195	70	1.0
115-3	13.98	0.2930	0.060	0.429	126	1.0
115-4	14.62	0.3503	0.100	0.684	144	1.0
115-5	13.67	0.6558	0.140	1.020	288	1.0
115-6	14.36	1.0365	0.250	1.740	433	1.7
115-7	14.60	2.0515	0.480	3.290	843	3.3
115-8	14.49	3.4946	0.810	5.590	1447	5.7
Bronze—Cu 89.8, Sn 9.7, Pb 0.5.						
79-1	16.00	0.1073	0.020	0.125	40	1.0
79-2	14.90	0.2279	0.040	0.268	92	1.0
79-3	14.70	0.3351	0.070	0.476	137	1.0
79-4	15.10	0.5086	0.110	0.728	202	1.0
79-5	14.65	0.7498	0.155	1.060	307	1.0
19-6	15.68	1.2086	0.260	1.660	462	2.0
79-7	15.28	2.3503	0.500	3.270	923	2.3
79-8	16.50	3.8189	0.810	4.900	1389	5.0

TABLE 6.—*Effect of variation in current density upon the corrosion rate of some metals and alloys in dilute sulphuric acid; duration of run, 4 hours.—Continued.*

Bronze—Cu 64.71, Sn 35.29.						
65-35-1	13.39	0.0268	0.11	0.822	12	1.0
65-35-2	14.69	0.4891	0.8	0.545	200	1.0
65-35-3	13.59	0.0939	0.270	1.987	41	3.9
65-35-4	15.01	0.1991	0.500	3.331	80	4.3
65-35-5	13.39	0.4234	0.810	6.050	190	5.7
65-35-x	14.59	0.1588	0.025	0.171	65	1.0
65-35-6	14.00	0.0211	0.095	0.680	9	...

TABLE 7.—*Effect of variation in current density upon the corrosion rate of naval brass (60.04:38.83:0.77 Cu-Zn-Sn) in several electrolytes; duration of run, 4 hours.*

Test piece number.	Immersed area, sq. cm.	Total loss in weight, grams.	Current, amperes.	Current density, amperes per sq. dcm.	Loss in mg. per sq. cm. per 24 hours.	Voltage drop, per cell.
Mine water from Edna No. 2 mine; free acidity, 2,020 p.p.m.						
22- 9	14.01	0.2464	0.025	0.178	106	1.75
22-13	14.85	0.4069	0.065	0.437	164	3.60
22-21	14.19	1.7743	0.420	2.960	750	17.00
22-25	14.21	2.4493	0.570	4.000	1034	27.00
22-29[a]	15.10	0.8852	0.570	3.780	1200	.....
Dilute sulphuric acid; 15,760 p.p.m.						
22-1	14.49	0.1040	0.020	0.138	43	1.00
22-2	14.57	0.1932	0.040	0.276	80	1.00
22-3	14.43	0.3312	0.070	0.484	138	1.00
22-4	14.92	0.5167	0.110	0.737	208	1.00
22-5	13.79	0.7584	0.155	1.120	330	1.00
22-6	14.77	1.2269	0.260	1.760	498	1.85
22-7	14.00	2.4848	0.490	3.500	1065	3.00
22-8	13.96	4.1610	0.810	5.800	1788	4.30
Sea water; 4 per cent NaCl.						
22-10	14.66	0.1575	0.025	0.171	65	1.40
22-14	13.50	0.4300	0.065	0.481	191	1.50
22-18	15.62	1.3454	0.200	1.280	516	2.30
22-22	14.01	2.2120	0.450	3.210	947	17.00
22-26	15.18	4.1095	0.610	4.020	1625	20.00
22-30[a]	15.07	1.1930	0.610	4.050	1620	.....
Sodium chloride solution; 8 per cent NaCl.						
22-11	14.73	0.1566	0.025	0.169	64	1.20
22-15	14.41	0.4314	0.065	0.450	180	1.40
22-19	15.44	1.3516	0.220	1.420	525	1.90
22-23	14.00	2.2280	0.450	3.210	955	2.90
22-27	14.00	2.5734	0.610	4.350	1103	10.00
22-32[a]	15.63	1.0335	0.610	3.900	1360	.....
1 per cent NaOH solution.						
22-12	14.15	0.0483	0.025	0.177	20	1.30
22-16	14.00	0.0765	0.065	0.465	33	1.40
22-20	15.10	0.2000	0.220	1.460	80	3.20
22-24	13.86	0.3203	0.450	3.240	139	5.00
22-28	13.82	0.4191	0.610	4.410	182	4.50
22-31[a]	14.65	0.1485	0.610	4.160	202	.....

[a] *This piece immersed for 1 hour and 10 minutes, the run being made to check the run immediately preceding.*

Table 5, 6 and 7 and Figures 3 and 4 show the effect of increasing current density on the corrosion loss of the several materials in the different eletrolytes. In some cases the loss is a

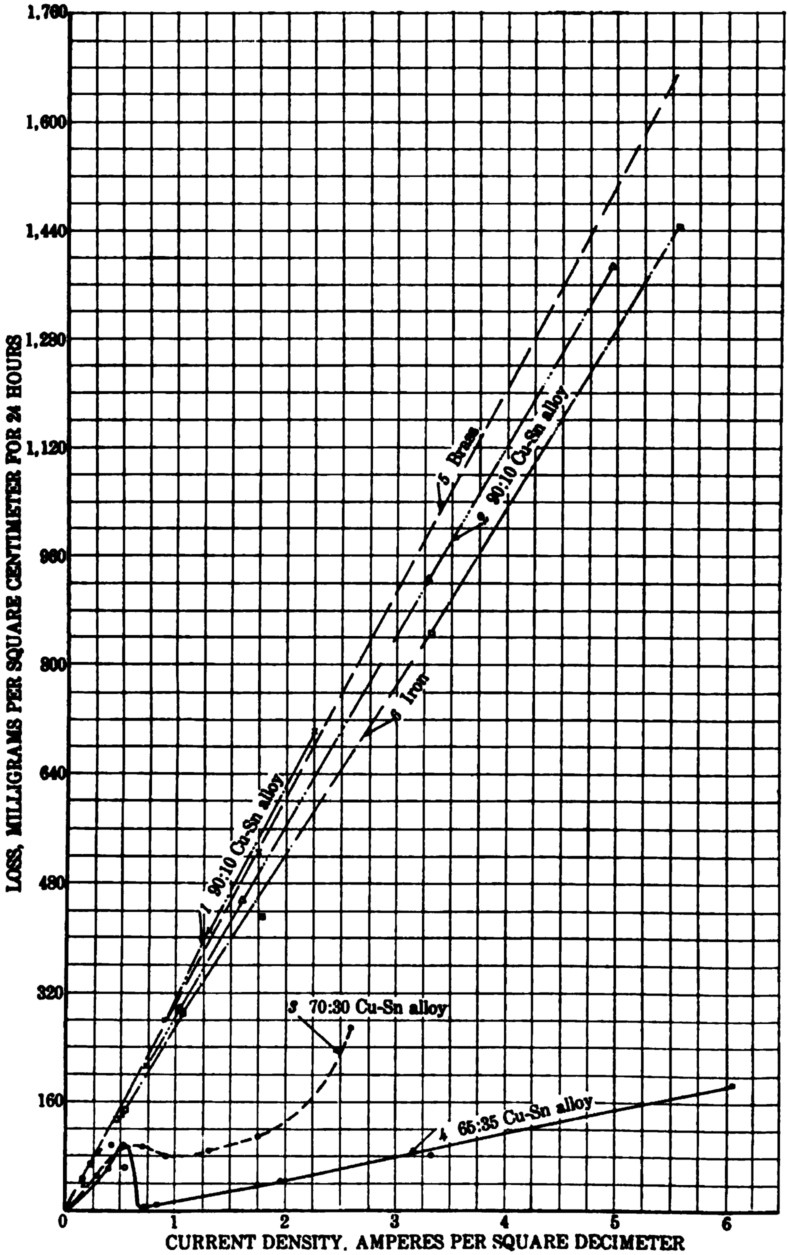

FIGURE 3.—*Effect of variation in current density upon the corrosion rate of some metals and alloys.*

straght-line function of the current density, while in others—the 70:30 and 65:35 copper-tin alloys, for example—this is not so, since the loss is affected by coating formation at higher current densities.

Since a low current density—0.2 amp. per sq. dcm., for example—gives sufficiently large loss in a fairly short time, and since at current density of less than 0.2 amp. the corrosion losses for all the materials tested in all the electrolytes are straight-line functions, it was decided to use this value in the additional tests. Variation of from 0.15 to 0.30 amp. is no doubt permissible. As will be seen from the graphs, it will no doubt be practical to corrode many alloys at higher current density than 0.2 amp., thus greatly accelerating the corrosion rate.

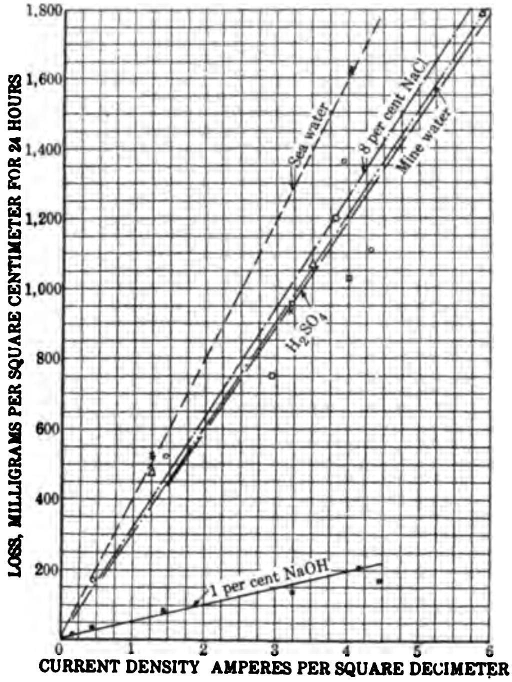

Figure 4.—*Effect of variation in current density upon the corrosion rate of naval brass in several electrolytes.*

TIME-PERIOD OF EXPOSURE.

Experiments were next made to determine the effect of time-period of exposure on the loss in weight in anodic corrosion. The 90:10 and 70:30 copper-tin alloys were corroded as before in 6.5

per cent sodium nitrate solution, using a current density of 0.179 amp. per sq. dcm., the time being varied over the range 15 minutes to 8 hours. The data are given in Table 8 and plotted in Figure 5. The loss in weight for these two alloys was found to be a linear function of the time. It should not be thought that the loss in weight by accelerated electrolytic corrosion is necessarily a linear function of the time, irrespective of the time, alloy, or electrolyte used, because of the formation of films or coatings. which may, in some cases, totally inhibit corrosion after a definite period. However, for testing purposes, the corrosion loss may in general be regarded as a linear function of the time within limits.

TABLE 8.—*Effect of variation in time of exposure on loss in weight for two alloys (constant current density of 0.179 amp. per sq. dcm.).*

Time, hours.	Total loss in weight, gram.	
	90:10 Cu-Sn alloy.	70:30 Cu-Sn alloy.
0.25	0.0059	0.0042
0.50	0.0130	0.0140
0.75	0.0208	0.0209
1.0	0.0296	0.0293
1.5	0.0396	......
2.0	0.0518	0.0534
4.0	0.1150	......
5.0	0.1275	0.1546
7.0	0.1692	0.2150
8.0	0.2051	0.2401

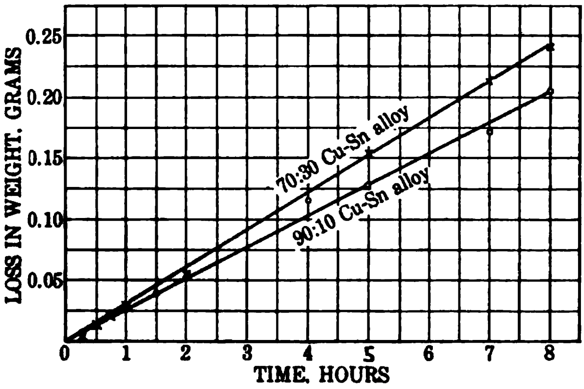

FIGURE 5.—*Loss in weight against time in anodic corrosion of 90:10 and 70:30 Cu-Sn alloys in sodium-nitrate solution.*

SHAPE OF TEST PIECES.

It was suggested during the course of the work that the shape of the test piece, for a given material, might have some effect on the loss in weight by accelerated elctrolytic corrosion. A number of runs were made to determine the effect of this factor, all other conditions being the same. Thus, test pieces in the shape of cylinders, rectangular parallelopipeds (where the width was half the thickness), square parallelopipeds, and thin sheets were tested, and it was found that the shape of the piece had no effect on the loss in weight.

TEMPERATURE.

Experiments on the effect of temperature on the loss in weight were not completed, but preliminary results indicated that the effect of increasing the temperature is to increase the loss. The experiments were not sufficiently numerous to determine the limits, if any, beyond which the corrosion rate would not increase. Published information on the effect of temperature is not conclusive.

SPEED OF ROTATION.

Experiments on the effect of speed of rotation of the test pieces were not completed, but apparently the effect of increasing the speed would be to increase the loss within limits.

GENERAL DISCUSSION OF ACCELERATED ELECTROLYTIC TEST.

Before taking up the technique of accelerated electrolytic corrosion testing in detail, and the correlation of accelerated test data with long-time immersion data, it is of interest to discuss briefly the above tests made to determine the most suitable conditions for carrying out the accelerated electrolytic test.

Taking up first the question of the accelerated electrolytic corrosion of metals and alloys in different electrolytes, the data secured on the corrosion of naval brass in five electrolytes show that the weight losses in the different electrolytes are comparable for current densities of less than about 0.2 amp. per sq. dcm. This value holds for all the electrolytes tested—sea water, 8 per cent sodium chloride, mine water, sulphuric acid, and 1 per cent sodium hydroxide—and at the higher current densities the graphs in Figure 4 show divergencies. These graphs show that for naval brass the corrosion rates in the electrolytes tested are straight-line functions at the lower current densities, but they are evidently not at the higher current densities. (Some of the plotted points do not lie on the curves as drawn.) It should not be thought that the loss for any material in a given solution will be the same as the loss for another material in the same solution, but rather that the different losses are directly proportional to the current density. Hence, if the same current density be employed in comparative tests of the corrosion rates of different materials in the same electrolyte, then the losses will be different in amount, but comparable. Different materials in the same electrolyte show irregularities in their loss-current density graphs at the higher current densities, owing to the formation of films and coatings at the higher current densities. The employment of a higher current density may, however, be desirable in making tests under specific conditions where it is ncessary to show the effect of coating formation.

It is of interest to give a summary of the observations made on the behavior of the electrolytes and the formation of precipitates therein, and of coatings formed on the test pieces. Observations were recorded for all runs, and those made in duplicating Curry's work are summarized in Table 9. In this table, the word "precipitate" refers to the actual precipitates formed in the electrolytes during test, while the term "coating" is employed to designate any corrosion products formed on the test pieces. At the conclusion of each run, the test pieces were removed from the electrolytes, rinsed with water, and cleaned with a rubber-tipped stirring rod in order to remove the corrosion products. The electrolytes were acidified with nitric acid in order to determine whether appreciable amounts of copper were present. The addition of nitric acid also causes the precipitation of insoluble tin salts, probably mostly stannic oxide. It was not possible to tabulate Curry's data in order to make comparison with those of the authors as to the behavior of the electrolytes and the formation of coatings, but in general the observations agree very well. Thus, in the case of the corrosion of the alloys in 6.5 per cent sodium-sulphate solution, Curry noted that the surface of the 90:10 Cu-Sn alloy tends to become tin-rich and a fine coating is formed. The authors noted similar characteristics in the case of the 88:12 Cu-Sn alloy. Curry also noted that the 65:35 Cu-Sn alloy corroded so slightly that there was no apparent change in the surface; the authors noted the same behavior in the case of the 67:33 Cu-Sn alloy.

TABLE 9.—*Observations on the character of precipitates formed in electrolytes and coatings formed on test pieces in the anodic corrosion of some copper-tin alloys. (See Tables 3 and 4.)*

Nominal composition of alloy, elements per cent.		Electrolyte, 6.5 per cent sodium sulphate.	Electrolyte, 6.5 per cent sodium chloride.	Electrolyte, 6.5 per cent sodium nitrate.	Electrolyte, 3 per cent ammonium oxalate plus 3 per cent oxalic acid.
Cu	Sn				
88	12	Gelatinous precipitate, changed color from blue to chocolate; considerable corrosion. Fine coating, removable with difficulty. Copper present in electrolyte.	Gelatinous precipitate, changed color from brownish yellow to dark brown. Thick coating, easily removable. Copper present in electrolyte.	Gelatinous precipitate, changed color from blue to chocolate. Coating easily removable, surface rough. Copper present in electrolyte.	No precipitate. Very small amount of corrosion. Deposit on cathode, probably copper plus small amount of tin. Copper present in electrolyte.
67	33	Precipitate formed, changed color from blue to greenish blue. No coating formed. No corrosion. Trace of copper in electrolyte.	Precipitate of three layers formed; colors blue, red, and yellow. Red coating over white coating, both easily removable. Trace of copper in electrolyte.	Precipitate formed, changed color from blue to greenish blue. Green coating over white coating. Surface pitted. Trace of copper in electrolyte.	Precipitate formed, color changed from blue to bluish green. Surface covered with light and dark spots. Considerable corrosion. Trace of copper in electrolyte.
30	70	Solution became milky, and white precipitate settled out gradually, followed by light blue coloration of solution. Very small amount of corrosion. Trace of copper in electrolyte.	Solution became milky, and white precipitate settled out gradually, followed by light blue coloration of solution. Thick coating, easily removable. Considerable corrosion. Trace of copper in electrolyte.	Solution remained clear. Very small amount of corrosion. Trace of copper in electrolyte.	Solution became milky, and white precipitate settled out gradually, followed by light blue coloration of solution. Considerable corrosion. Coating easily removable. Trace of copper in electrolyte.
11	89	Solution became milky, and heavy white precipitate settled out gradually. Slight corrosion. No copper in electrolyte.	Solution became milky, and heavy white precipitate settled out gradually. Some corrosion. Nodules formed on surface. No copper in electrolyte.	Solution became milky, and heavy white precipitate settled out gradually. Considerable corrosion, and some pitting. No copper in electrolyte.	Clear solution. Deposit on cathode. Corrosion irregular. No copper in electrolyte.

Observations similar to those recorded in Table 9 were also made in connection with the experiments summarized in Tables 6 and 7, but owing to the confines of space these cannot be taken up in detail here. However, a few remarks on the general nature and more prominent characteristics noted in connection with the behavior of the electrolytes and the coatings formed may be given.

When copper and the brasses were corroded in dilute sulphuric acid (see Table 6), it was found, as would be expected, that increasing amounts of copper were deposited on the cathode with increasing current density. At the lower current densities the electrolytes were light blue in color, and small quantities of copper were deposited on the cathode. The anodes assumed a characteristic red copper coating, which was probably left *in situ* for the brasses, since the zinc corroded at a more rapid rate than the copper. There is some evidence (based on microscopic study) that the copper was re-deposited, but this evidence is not conclusive except in the case of the brasses of, or near, alpha + gamma in composition, and then only at the higher current densities. That is to say, copper was re-deposited, but this evidence is not conclusive except in group 16, high brass, and group 22, naval brass (see Table 7). Figure 6 is a photomicrograph of corroded test piece No. 22-5, in which deposited copper is replacing the zinc-rich gamma. For all of the copper-rich materials, the formation of large trees of copper at the cathode was characteristic of corrosion in sulphuric acid. Iron formed trees of iron on corrosion at the higher current densities, but at the lower current densities the electrolyte was fairly clear.

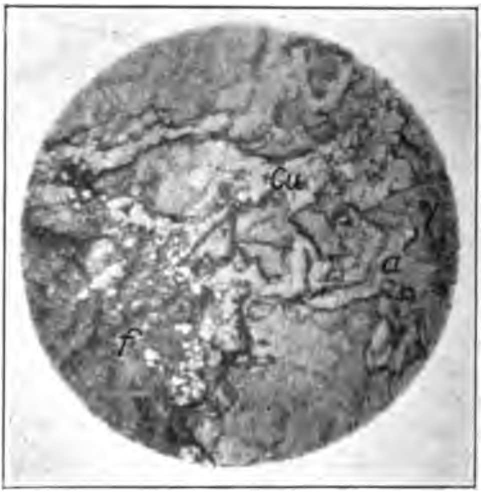

FIGURE 6.—*Copper replacing gamma in a naval brass corroded at high current density.*

The behavior of the copper-tin alloys in dilute sulphuric acid is interesting. The 90:10 Cu-Sn alloy gave a black coating on the anode within a few minutes after starting a run, and this seemed to retard the corrosion rate. After removing this black coating by cleaning in water a grey coating was noticed on the test pieces which had been corroded at current densities higher than 0.476 amp. per sq. dcm.—that is, the grey coating was first noticed on cleaning test-piece No. 79-4. (See Table 6.) The black coatings on the different test pieces were easily removable, but the grey coatings adhered firmly. These latter were evidently largely stannic oxide. Figure 7 shows the group of 90:10 Cu-Sn alloy test pieces after corrosion in dilute sulphuric acid. The pieces are arranged in order form left to right for increasing current density (see Table 6), and show the variation of coatings formed. Figure 8 is a macrograph of part of test-piece No. 79-8, showing the structure of the coating of stannic oxide.

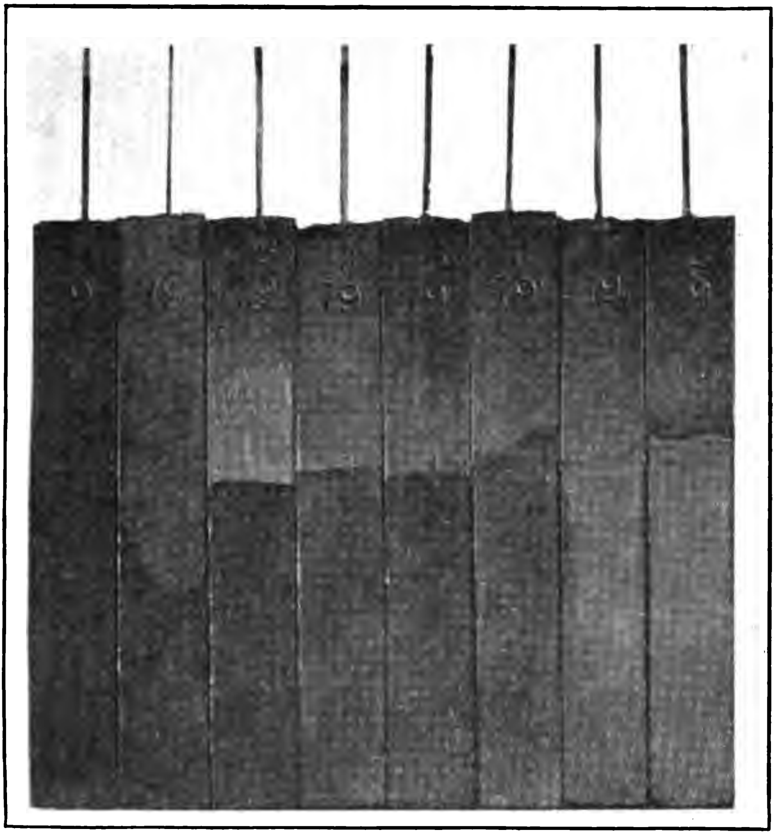

FIGURE 7.—*Group of 90:10 CuSn alloy test pieces corroded in dilute sulphuric acid; after cleaning; increasing current density, left to right.*

The 65:35 copper-tin alloy corroded in a peculiar manner. At current densities below 0.5 amp. per sq. dcm., no coatings were formed on the test pieces, and at this current density, and above,

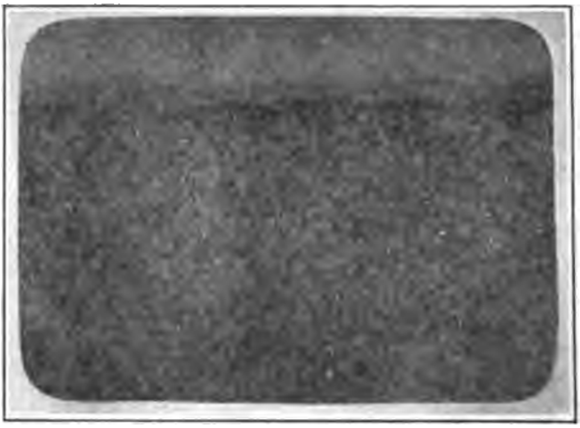

FIGURE 8.—*Macrograph of 90:10 Cu-Sn alloy corroded in dilute* H_2SO_4*; current density 5.05 amps. per sq. dcm.*

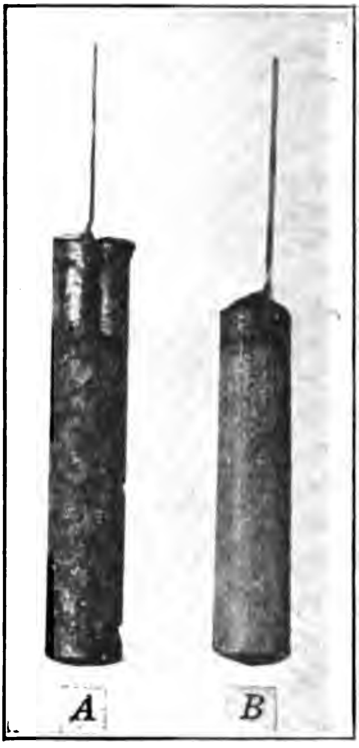

FIGURE 9.—*Surface aspect of 65:35 Cu-Sn alloy; A, corroded at low current density; B, at high current density; in dilute sulphuric acid.*

the corrosion rate fell off sharply. This was also true of the 70:30 Cu-Sn alloy when corroded in 6.5 per cent sodium-nitrate solution, but the drop in rate was not so abrupt. The two lowest graphs of Figure 3 illustrate this point. Examination of the test pieces of these alloys showed that a coating of some greyish white material, presumably stannic oxide, had been formed. The effect of low and high-current densities upon the corrosion of the 65:35 Cu-Sn alloy (and the coatings formed) is shown clearly in Figure 9 *A* and *B*. *A* shows the appearance of a test piece after corroding at low-current density, while *B* shows another test piece after corroding at high-current density. In the former, the surface is etched, but no coating has been formed, while in the latter a grey coating of stannic oxide has developed on the surface. Figure 10 is a macrograph of the surface shown in Figure 9 *A*, and it is clear from this that no coating is present. Consideration of the curves of Figure 3 and microscopic examination proves that a true protective coating is formed on this alloy at high-current density.

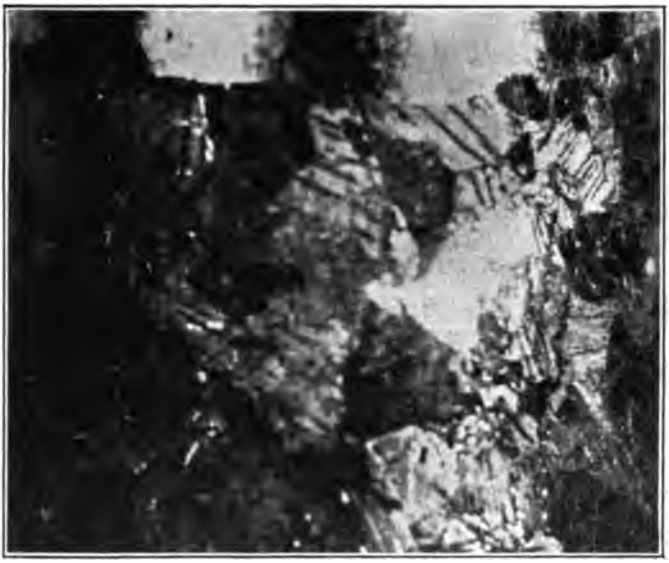

FIGURE 10.—*Macrograph of surface shown in Figure 9*A.

In the case of the corrosion of naval brass in several electrolytes (see Table 7), it was found that the corrosion characteristics were those typical of corrosion of brass in dilute sulphuric acid, as previously explained. These characteristics are also typical of brass corrosion in mine water, except that such water is hydrolyzed, and a brown precipitate of iron salts is formed. In sea water and salt water, large quantities of precipitate are formed, orange-colored precipitates predominating. Coatings which are easily removable are formed on the anode, and these vary in color and thickness. A varying amount of copper is deposited on the anode and the cathode, increasing with increasing current density, and the deposited copper on the anode may be corroded at the higher current densities. Apparently, also, deposited copper crystals may grow under the coatings.

SUMMARY OF RESULTS OF ACCELERATED ELECTROLYTIC TEST.

The results of the preliminary tests may be summarized as follows:

1. Consideration of the tabular matter and plotted graphs, together with information obtained from microscopic examination, shows that accelerated electrolytic tests may be duplicated by independent workers, as has been done by the authors in checking Curry's work. The effects of the variable factors which influence results have been examined, and it is shown that a low current density, say 0.2 amp. per sq. dcm., is suitable. Higher current densities may be better in specific cases. In considering relative corrosion losses among different metals and alloys in the same solutions or for given metals and alloys in different solutions, all variable factors must be controlled; and all important observations as to the behavior of electrolytes and the formation of coatings must be properly correlated. It should be pointed out that true corrosion loss-in-weight results should be expressed in terms of the equivalents of the metals compared. Thus, the rate of one metal may be faster than that of another, but the actual loss less, because of difference in the atomic weights. The rate of corrosion should properly be expressed in such terms that difference in mol weights, solution pressures, polarization, and other factors will be properly accounted for.

2. The experiments described lead to a statement of the method which the authors believe is best suited to testing in acid mine water. This is given in the following discussion.

TECHNIQUE OF ACCELERATED ELECTROLYTIC TESTING.

The electrolytic apparatus to be employed for making accelerated electrolytic tests may be of very simple construction, and the apparatus developed by the Bureau of Mines for such tests is shown in Figure 11, while the wiring diagram is shown in Figure 12. However, any simple type of apparatus for electrolytic analysis with rotating spindles may be employed, and as many cells as are desired can be used. The apparatus is equipped with 12 rotating anode connections, and these may be used independently or all together as desired. It is ordinarily necessary to maintain the speed of rotation constant for groups of runs, and some speed-controlling device should be employed. Thus, the rotating anode spindles may be driven by a variable-speed motor, or the speed of a constant-speed motor can be varied by a rheostat. The former arrangement is preferable. The imposed current is passed through the cells in series, and this is regulated through a lamp-bank resistor. The cells are heavy-walled glass beakers, of 500 c.c., or more, capacity. The cathodes are platinum wires.

Samples for test are cut to any convenient size, and in the preliminary work an area of about 14 sq. cm. has been employed for exposure to the corroding medium. The weight of the test piece may be as much as 60 grams. The surface of the test piece should be in the same condition as it is to be when used in service—that is to say, if a bronze is to be used as a machined part in a mine pump, the test piece should be machined; or if a rough sand casting is to be used in service, the test piece should be a rough cast specimen. The test piece should be run for a sufficient period to yield a weighable loss; in the case of very non-corrodible materials, experience has shown that a period of 8 hours is long enough to determine their corrodibility. Most industrial metals and alloys will show a decided loss in 8 hours. The time-factor will depend also upon the nature of the electrolyte, which should be the same as the corroding medium (or comparable with it) in which the metal or alloy is to be used in service. Accurate record should be kept of the weight of the test piece before and after corrosion, the area of the exposed portion, the current imposed, the voltage-drop per cell, the chemical analysis of the test piece, the chemical analysis of the electrolyte, and the nature of the coatings and precipitates formed. It is desirable to analyze the coatings and electrolytes after corrosion. After cleaning the test pieces, which can be best accomplished by rubbing with a stiff bristle brush in running water, and then drying, careful visual and microscopic examination should be made of corroded samples.

There are several precautions which should be taken in carrying out accelerated electrolytic tests, and a few of these may be noted briefly here:

First—the speed of rotation should be the same in testing different materials for comparison, and attempt might well be made to approximate, by variation of speed, the rate of flow in service. If materials are exposed in service to stationary corroding media, the electrolytic test might be made with stationary anodes. The

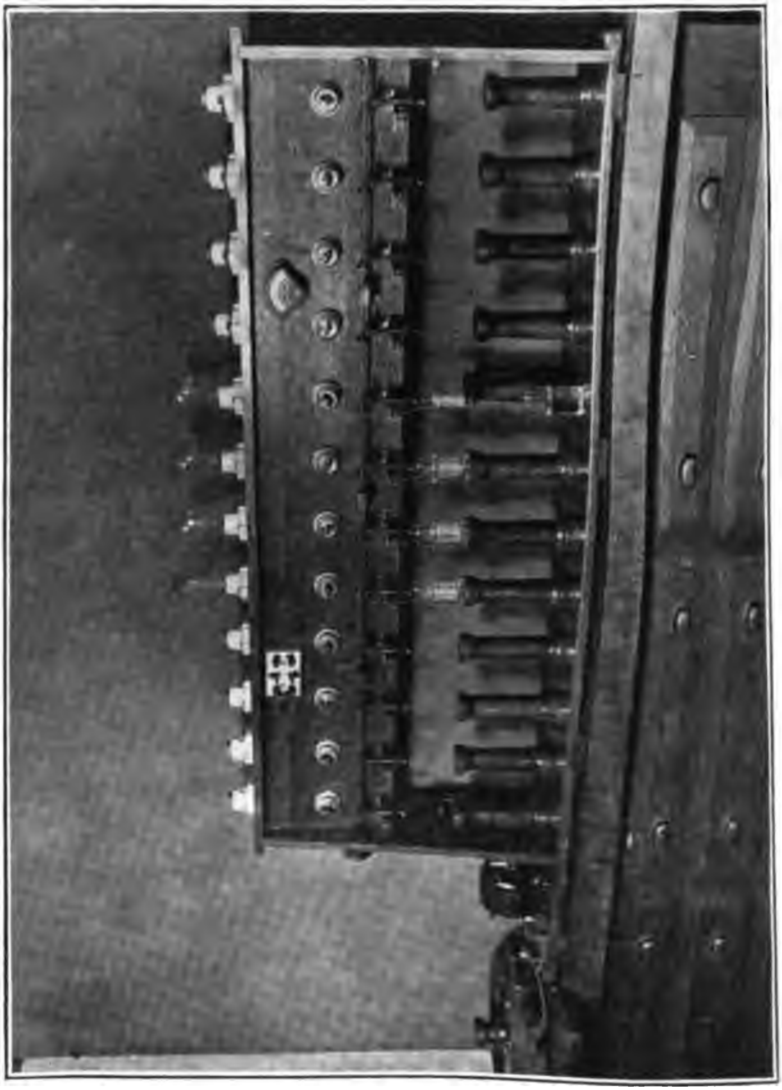

Figure 11.—*Electrolytic cabinet for accelerated corrosion testing; Bureau of Mines model.*

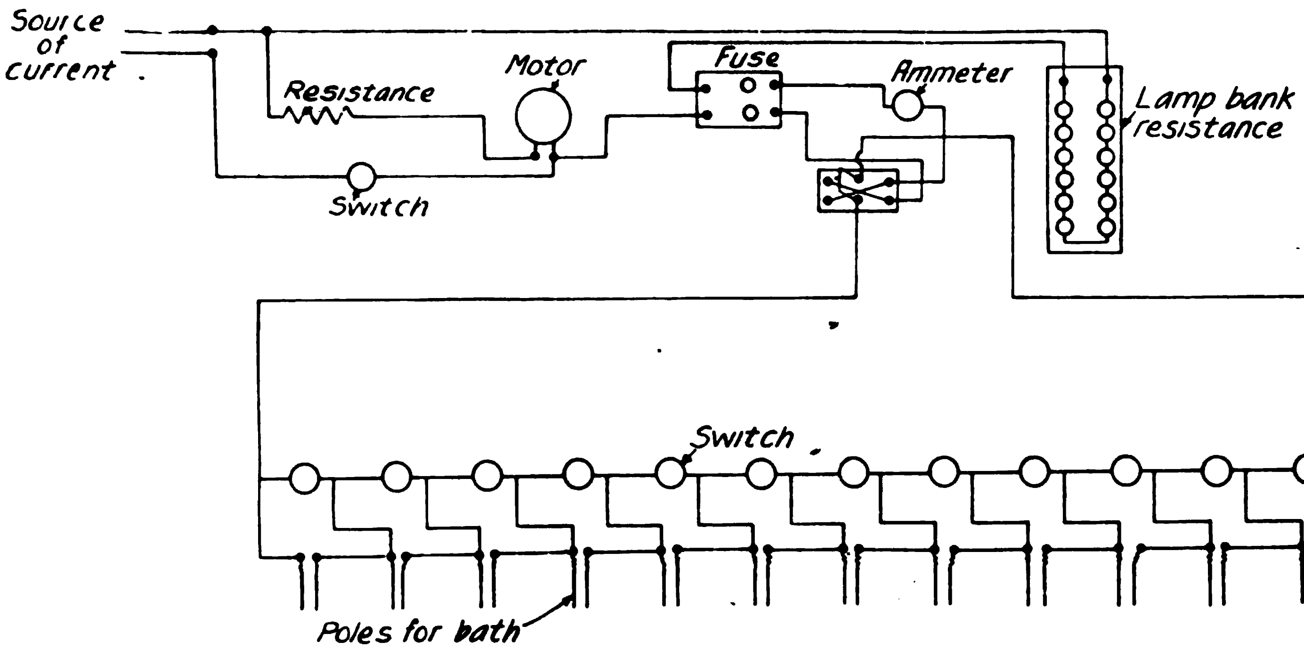

FIGURE 12.—*Wiring diagram of the apparatus of Figure 11.*

rate of flow has a marked effect on corrosion, as has been shown by Dieterlen[30], among others. Rate of flow can be duplicated by the speed of rotation in the accelerated test.

Second—the temperature should be constant, since temperature variation has a marked effect on corrosion losses; the service temperature should be employed.

Third—care should be taken in choosing the corroding medium; in the test, the corroding medium should be the same as that encountered in service so that the conditions of the medium, such as catalysts, organic matter, metal salts, and the combination of these, will be the same as those met with in actual working conditions. As further precaution, care must be taken in sampling the liquid that a representative sample be secured.

Fourth—the current density per unit of area exposed should be the same for samples being tested; small change in current density causes considerable difference in the weight loss.

Correlation of accelerated electrolytic tests and long-time immersion tests were made in the case of 42 metals and alloys corroded in acid mine water, and the results are given in the following section.

CORRELATION OF LONG-TIME IMMERSION TESTS AND ACCELERATED TESTS IN ACID MINE WATERS.

The development of the accelerated electrolytic corrosion test and the effects of variable factors on corrosion rates in this test have been discussed in preceding pages of this bulletin, and it remains now to take up the application of the test to practical corrosion problems. It will be shown that the results obtained in a few hours by this test are comparable in most cases to long-time immersion test results obtained after months in a corroding medium. Most of the metals and alloys tested in the long-time immersion runs made by Selvig[31] and one of the writers were later tested by the accelerated electrolytic corrosion method. The materials omitted were the group of high-silicon cast irons, and these were left out because of the difficulty in preparing suitable test pieces from material in hand.

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[30] Dieterlen, H., Quelque idees sur les economisseurs en acier: Chaleur et Industrie, vol. 28, 1922, pp. 1515-1521.

[31] Selvig, W. A., and Enos, G. M., work cited.

The accelerated electrolytic tests on the metals and alloys were run in three electrolytes—namely, (1) Edna No. 2 mine water, free acidity 2,050 p.p.m., and total acidity 16,660 p.p.m.; (2) Montour No. 1 mine water, free acidity 410 p.p.m., and total acidity 6,500 p.p.m.; and (3) Calumet mine water, free acidity 410 p.p.m., and total acidity 1,300 p.p.m. (all in terms of sulphuric acid). The following factors were held constant within small limits; speed of rotation of test pieces, 140 r.p.m.; temperature, 20 to 25° C. (ordinary room temperature); current imposed, 0.025 amp.; area submerged, 14 sq. cm.; and time-period of test, 8 hours.

DATA ON CORROSION IN THE EDNA NO. 2 MINE WATER.

A series of tests was made on 42 metals and alloys in Edna No. 2 mine water, running 12 pieces in series. Table 10 gives the results obtained in the accelerated electrolytic tests with the comparative figures on the long-time exposure tests. The current throughout was maintained constant at 0.025 amp., the current density showing slight variations—namely, ± 0.01 amp. per sq. dcm.—due to slight differences in area.

The average loss in milligrams per square centimeter per 24 hours for both the long-time exposure and the accelerated electrolytic tests is plotted in Figure 13 for each individual alloy. In this way a direct comprehensive comparison can be drawn between the two tests. It should be pointed out that in constructing this figure, the actual values for the losses in weight in the long-time exposure test are plotted but only one-tenth of the actual values for the accelerated electrolytic test. This was done so that the two curves of the graph would lie relatively close together.

TABLE 10.—*Comparative loss in weight of test pieces in accelerated electrolytic corrosion test, and long-time immersion test, for 42 metals and alloys in Edna No. 2 mine water.*

Test piece number.[a]	Designation.	Chemical composition, per cent.[b]	Area of test piece, sq. cm.	Weight in grams.		Loss in weight, gram.	Loss per sq. cm. per 24 hours in accelerated test, milligrams.	Loss per sq. cm. per 24 hours in long-time exposure tests,[d] milligrams.
				Before immersion.	After immersion.			
		Brasses.						
16-a 16-b	Rolled high brass	[c]Cu 66.55 Zn 33.45	13.94 13.94	8.3854 8.9195	7.9962 8.5251	0.3892 0.3944	83.7 84.9	....
Average			.....	......	......	......	84.3	7.30
19-a 19-b	Rolled low brass	[c]Cu 80.09 Zn 19.91	13.96 13.97	8.7062 8.0859	8.3600 7.7083	0.3462 0.3776	74.5 81.1	....
Average			.....	......	......	......	77.8	7.17
22-a 22-b	Rolled naval brass	[c]Cu 60.4 Zn 38.83 Sn 0.77	14.00 13.98	9.0955 8.4606	8.7582 8.1082	0.3373 0.3524	72.3 75.8	....
Average			.....	......	......	......	74.1	7.11
28-a 28-b	Rolled brass (Admiralty metal), grain size 0.025 mm.	Cu 70.80 Zn 28.06 Sn 1.14	13.98 13.97	9.3006 9.5075	8.9739 9.1462	0.3267 0.3613	70.2 77.6	....
Average			.....	......	......	......	73.9	7.07
64-a 64-b	Rolled brass (Admiralty metal), grain size 0.035 mm.	Cu 71.38 Zn 27.36 Sn 1.26	13.98 13.97	9.0871 9.4897	8.7429 9.1332	0.3442 0.3565	74.0 76.5	....
Average			.....	......	......	......	75.3	6.80
67-a 67-b	Rolled brass (Admiralty metal), grain size 0.075 mm.	Cu 71.46 Zn 27.42 Sn 1.12	13.96 13.95	9.8311 9.6915	9.4567 9.3158	0.3744 0.3757	80.5 80.7	....
Average			.....	......	......	......	80.6	6.72
46-a 46-b	Rolled manganese brass	Cu 57.95 Sn 0.47 Zn 41.02 Pb trace Fe 0.55	14.01 14.02	11.5262 10.9011	11.2066 10.5861	0.3196 0.3150	68.3 67.4	....
Average			.....	......	......	......	67.9	6.66

Bronzes.

79-a	Cast bronze	Cu 89.8 Sn 9.7 Pb 0.5	13.97	23.5448	23.3728	0.1720	37.0	....
79-b			13.95	22.1126	21.9375	0.1751	37.8	....
Average			.....	......	......	......	37.4	2.12
55-a	Rolled bronze	Cu 98.51 Sn 1.49	13.98	9.4695	9.1344	0.3351	72.0	....
55-b			13.95	9.6174	9.2577	0.3597	77.3	....
Average			.....	......	......	......	74.7	7.03
58-a	Rolled phosphor bronze	[c] Cu 94.4 Sn 5.5 P 0.1	14.01	8.9089	8.6077	0.3012	64.4	....
58-b			14.03	9.2130	8.9067	0.3063	64.5	....
Average			.....	......	......	......	64.5	4.80
49-a	Rolled zinc-phosphor bronze	Cu 89.8 Pb 4.6 Sn 5.6 Fe trace P trace	13.96	11.1504	10.7887	0.3617	77.6	....
49-b			14.07	12.0086	11.6558	0.3528	75.4	....
Average			.....	......	......	......	76.5	1.82
73-a	Cast lead-zinc bronze	Cu 86.34 Sn 11.24 Pb 0.83 Zn 1.60	13.98	20.5431	20.3666	0.1765	37.9	....
73-b			13.96	18.8258	18.6569	0.1689	36.3	....
Average			.....	......	......	......	37.1	0.83
85-a	Cast lead bronze	Cu 74.9 Pb 14.3 Sn 10.5	13.99	19.2448	19.0798	0.1650	35.4	....
85-b			14.00	12.8034	12.6320	0.1714	36.6	....
Average			.....	......	......	......	36.0	1.21
82-a	Cast lead bronze	Cu 87.5 Sn 10.6 Pb 1.6	14.01	23.0347	22.8364	0.1983	42.7	....
82-b			13.97	21.9898	21.7949	0.1949	41.5	....
Average			.....	......	......	......	42.1	2.56

[a] *Test piece numbers used are the same as those used in Bulletins 4 and 5, Coal-Mining Investigations, Carnegie Inst. of Technology, 1922-1923.*

[b] *Analyses, unless otherwise noted, were run by C. H. Eldridge and G. B. Dalrymple.*

[c] *Analysis furnished by co-operating company.*

[d] *Average figures are obtained from Bull. 4, Coal-Mining Investigations, Carnegie Inst. of Technology, 1922.*

TABLE 10.—*Comparative loss in weight of test pieces in accelerated electrolytic corrosion test, and long-time immersion test, for 42 metals and alloys in Edna No. 2 mine water.—Continued.*

Test piece number.[a]	Designation.	Chemical composition, per cent.[b]	Area of test piece, sq. cm.	Weight in grams.		Loss in weight, gram.	Loss per sq. cm. per 24 hours in accelerated test, milligrams.	Loss per sq. cm. per 24 hours in long-time exposure tests,[d] milligrams.
				Before immersion.	After immersion.			
		Cupro-nickel.						
37-a	Rolled cupro-nickel (coin metal)	Cu 74.60 Ni 25.40	14.04	9.3700	9.0505	0.3195	68.2	....
37-b			13.98	9.2146	8.8855	0.3291	70.6	....
Average			.....	......	......	......	69.4	7.34
31-a	Rolled cupro-nickel	Cu 84.36 Ni 15.64	14.01	9.1140	8.7916	0.3224	69.0	....
31-b			14.02	8.8536	8.5368	0.3168	67.8	....
Average			.....	......	......	......	68.4	7.44
1-a	Cast lead cupro-nickel	Cu 53.57 Fe 0.61 Sn 0.56 Ni 25.30 Pb 19.58	14.00	47.0935	46.8166	0.2769	59.4	....
1-b			14.01	44.8712	44.6212	0.2500	53.5	....
Average			.....	......	......	......	56.5	4.19
4-a	Cast chromium-iron cupro-nickel	Cu 42.24 Ni 35.00 Fe 9.35 Cr 11.89 Si 1.50	13.94	45.4226	45.1326	0.2900	62.4	....
4-b			13.94	45.8286	45.5154	0.3132	67.4	....
Average			.....	......	......	......	64.9	6.58
112-a	Cast iron-manganese cupro-nickel	Cu 71.16 Ni 19.01 Mn 2.35 Fe 7.47	13.98	21.2147	20.9373	0.2774	59.5	....
112-b			13.94	19.8738	19.5708	0.3030	65.2	....
Average			.....	......	......	......	62.4	7.27

			Nickel silver.					
13-a	Rolled nickel silver	[c]Cu 63.78 Zn 17.68 Ni 18.54	14.03	8.9526	8.6017	0.3509	75.0	....
13-b			13.99	8.8299	8.4969	0.3330	71.5	....
Average			.....	......	......	......	73.3	7.16
43-a	Rolled iron-nickel silver	Cu 66.03 Zn 23.99 Ni 9.92 Fe 0.05	14.00	8.9694	8.5844	0.3850	82.5	....
43-b			13.85	8.9937	8.6088	0.3849	83.3	....
Average			.....	......	......	......	82.9	7.56
34-a	Rolled nickel silver	Cu 52.79 Zn 34.58 Ni 12.63	14.04	8.5847	8.1785	0.4062	86.9	....
34-b			14.02	9.7871	9.3809	0.4062	87.0	....
Average			.....	......	......	......	87.0	7.28
10-a	Cast silicon-nickel silver	Cu 72.3 Ni 16.5 Sn 3.5 Zn 7.4 Pb 0.3 Si trace	13.98	18.9700	18.6756	0.2944	63.2	....
10-b			13.94	18.6273	18.3825	0.2448	42.6	....
Average			.....	......	......	......	57.9	6.98
7-a	Cast tin-lead nickel silver	Cu 63.52 Ni 12.85 Sn 4.59 Zn 11.55 Pb 7.49	13.98	25.5543	25.2777	0.2766	59.5	....
7-b			13.98	21.9874	21.7511	0.2363	50.8	....
Average			.....	......	......	......	55.2	4.24
136-a	Cast tin-lead nickel silver	Cu 54.32 Pb 6.30 Sn 2.54 Zn 16.33 Ni 20.51	14.05	51.0765	50.7214	0.3551	75.8	....
136-b			13.96	51.8583	51.4907	0.3676	79.0	....
Average			.....	......	......	......	77.4	4.60
			Aluminum alloys.					
88-a	Cast aluminum-silicon alloy	Si 3.90 Al 96.1 (by difference)	13.97	11.9329	11.8573	0.0756	16.2	....
88-b			14.01	13.3714	13.2958	0.0756	16.2	....
Average			.....	......	......	......	16.2	2.20
91-a	Cast aluminum-manganese alloy	Mn 1.81 Al 98.19 (by difference)	14.00	13.2254	13.1230	0.1024	22.0	....
91-b			14.00	12.3927	12.2919	0.1008	21.6	....
Average			.....	......	......	......	21.8	2.23

[a] *Test piece numbers used are the same as those used in Bulletins 4 and 5, Coal-Mining Investigations, Carnegie Inst. of Technology, 1922-1923.*

[b] *Analyses, unless otherwise noted, were run by C. H. Eldridge and G. B. Dalrymple.*

[c] *Analyses furnished by co-operating company.*

[d] *Average figures are obtained from Bull. 4, Coal-Mining Investigations, Carnegie Inst. of Techonology, 1922.*

TABLE 10.—*Comparative loss in weight of test pieces in accelerated electrolytic corrosion test, and long-time immersion test, for 42 metals and alloys in Edna No. 2 mine water.—Continued.*

Test piece number.[a]	Designation.	Chemical composition, per cent.[b]	Area of test piece, sq. cm.	Weight in grams.		Loss in weight, gram.	Loss per sq. cm. per 24 hours in accelerated test, milligrams.	Loss per sq. cm. per 24 hours in long-time exposure tests,[d] milligrams.
				Before immersion.	After immersion.			
		Aluminum alloys—Continued.						
94-a 94-b	Rolled aluminum-manganese alloy	Mn 0.95 Si 0.53 Fe 0.95 Al 97.57 (by difference)	13.92 13.77	3.5619 3.3678	3.4335 3.2413	0.1284 0.1265	27.6 27.6	....
Average			.....	......	......	......	27.6	1.76
97-a 97-b	Rolled aluminum alloy	Cu 3.62 Fe 0.45 Mn 0.46 Si 0.56 Al 94.91 (by difference)	14.03 13.96	3.4720 3.4674	3.3909 3.3856	0.0811 0.0818	17.4 17.6	....
Average			.....	......	......	......	17.5	1.73
		Rustless steels.						
106-a 106-b	Rolled high chromium steel	Cr 29.5 Mn 0.27 Si 0.55 C low Fe remainder	14.00 13.98	9.8948 9.9052	9.8217 9.8355	0.0731 0.0697	15.7 15.0	....
Average			.....	......	......	......	15.4	0.00022
100-a 100-b	Rolled rustless steel "A"	Ni 23.87 Cr 12.96 Si 3.40 C low Fe remainder	13.98 14.01	10.6067 9.6819	10.5219 9.5940	0.0848 0.0879	18.2 18.7	....
Average			.....	......	......	......	18.5	0.00022
103-a 103-b	Rolled rustless steel "B"	Ni 29.60 Cr 10.73 Si 3.26 C low Fe remainder	13.96 13.97	10.2522 10.4171	10.2251 10.3868	0.0371 0.0303	5.8 6.5	....
Average			.....	......	......	......	6.15	0.00044
		Miscellaneous metals and alloys.						
115-a 115-b	Rolled ingot iron	[c]Fe 99.9	13.93 13.98	7.7169 7.9368	7.3858 7.6026	0.3311 0.3342	71.2 71.9	....
Average			.....	......	......	......	71.6	7.14

Miscellaneous Metals and Alloys.—Continued.

109-a	Rolled aluminum	[c]Commercially pure aluminum	13.95	3.4326	3.3077	0.1249	26.8	....
109-b			13.98	3.4876	3.3562	0.1814	28.2	....
Average			.....	......	......	......	27.5	1.56
121-a	Rolled nickel	[c]Ni 99+	13.93	9.8384	9.5956	0.2428	52.2	....
121-b			13.74	9.2226	8.9749	0.2477	54.0	....
Average			.....	......	......	......	53.1	7.06
76-a	Cast aluminum bronze	Cu 93.9 Al 6.1 (by difference)	13.95	19.7432	19.4351	0.3081	66.4	....
76-b			14.05	14.5436	14.2911	0.2525	54.0	....
Average			.....	......	......	......	60.2	5.08
52-a	Rolled iron-aluminum bronze	Cu 86.23 Fe 4.81 Al 8.96 (by difference)	13.99	10.2074	9.9225	0.2849	61.1	....
52-b			14.01	10.2465	9.9690	0.2775	59.4	....
Average			.....	......	......	......	60.3	5.98
70-a	Cast copper-lead alloy	Cu 53.4 Pb 46.4	13.93	44.5236	44.2759	0.2477	53.4	....
70-b			13.99	29.7853	29.5419	0.2434	52.2	....
Average			.....	......	......	......	52.8	3.87
40-a	Rolled monel metal	Ni 65.1 Cu 30.52 Fe 4.2	13.98	11.4879	11.1633	0.3246	69.7	....
40-b			13.98	11.2197	10.9057	0.3140	67.5	....
Average			.....	......	......	......	68.6	6.68
61-a	Rolled copper-manganese-iron alloy	Cu 94.81 Mn 4.52 Fe 0.67	14.01	9.3856	9.0581	0.3275	70.1	....
61-b			14.02	8.4176	8.0641	0.3535	75.6	....
Average			.....	......	......	......	72.85	7.36
139-a	Rolled nickel-chromium-iron alloy	Ni 52.50 Cr 9.29 Mn 1.24 Al 0.20 Si 0.19 Fe remainder	13.97	11.4498	11.3314	0.1184	25.4	....
139-b			13.98	12.3374	12.2360	0.1014	21.8	....
Average			.....	......	......	......	23.6	7.35
118-a	Rolled nichrome	Ni 57.44 Cr 9.37 Si 0.55 Mn 1.75 Fe remainder	14.01	9.9977	9.8676	0.1301	27.9	....
118-b			13.98	9.6479	9.5210	0.1269	27.2	....
Average			.....	......	......	......	27.55	0.026

[a] *Test piece numbers used are the same as those used in Bulletins 4 and 5, Coal-Mining Investigations, Carnegie Inst. of Technology, 1922-1923.*

[b] *Analyses, unless otherwise noted, were run by C. H. Eldridge and G. B. Dalrymple.*

[c] *Analyses furnished by co-operating company.*

[d] *Average figures are obtained from Bull. 4, Coal-Mining Investigations, Carnegie Inst. of Techonology, 1922.*

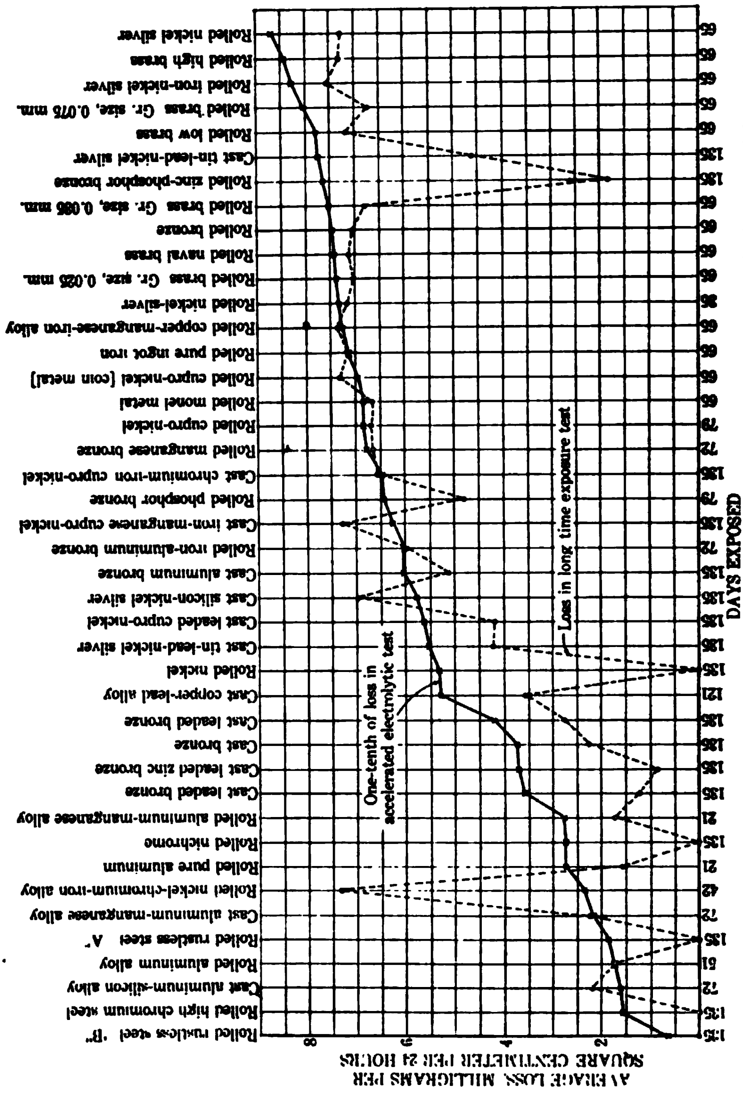

FIGURE 13.—*Comparison of corrosion losses in the accelerated electrolytic test with losses in the long-time immersion test in Edna No. 2 mine water.*

On examination of the figure it is seen that the curve for the electrolytic test takes roughly the same slope as the one for the long-time exposure. The chief discrepancies are found in the case of the following five materials: cast lead-zinc bronze, rolled nickel, rolled zinc-phosphor bronze, rolled nichrome, and rolled nickel-iron-chromium alloy. Some of these exceptions can be explained on the basis of the protective coatings formed. For the first three alloys just mentioned it was found that the losses in the long-time exposure test are much smaller than those in the accelerated test. Test pieces of these alloys were exposed in the mine water for 135 days. It is certain that after a definite period of time a protecting coating was formed on each of these pieces. After the formation of this coating, the rate of corrosion was changed—that is, it was greatly reduced—but neither the rate of corrosion nor reduction of this rate is necessarily a linear function of the time-period. In the accelerated electrolytic test, the pieces were all run for the same period—namely, 8 hours—while in the long-time test the exposure periods varied from 21 days to 135 days, as shown in Figure 13. It is, of course, obvious that the exact relation between the time necessary to secure comparable losses and comparable coatings in both tests is not known on the basis of the present data, and this would necessarily differ for different metals and alloys. Hence, it is not surprising that where protective coatings are formed, as in the case of these three alloys, there should be considerable variation in the result of the two tests. It is probable that had the accelerated electrolytic tests for these alloys been run for longer periods, or if the current density had been higher, the effects of protective coatings would have been made evident in the results, and agreement between the two tests would have been close.

In the case of nichrome, the discrepancy, although marked, is not so great as for the other alloys. It seems quite possible that a protective film may have been formed in the long-time tests, which did not form in the accelerated test. A film, as defined by the authors, would not be visible, and hence would not be noted in the results of the long-time test.

In the case not previously explained—that is, the rolled nickel-chromium-iron alloy—the greater relative loss in the long-time test is explained by non-homogeneity of the material, as was shown by microscopic examination.

Microscopic examination of the alloys which yielded less loss in the long-time test showed that protective coatings had been formed; no coating was formed on the nickel-chromium-iron alloy.

It would naturally be expected that a conversion factor for translating the results of accelerated electrolytic tests into terms of long-time immersion tests should be obtainable, and the data of Table 10 indicate that the acceleration in the electrolytic test is of the order of 10 times over the ordinary immersion test, depending upon the material, the time-period of exposure, and other circumstances.

DATA ON CORROSION IN THE CALUMET MINE WATER.

A series of tests was next made using Calumet mine water for the electrolyte, and 12 selected alloys from the group of 42 tested in Edna No. 2 mine water. The alloys were selected to yield representative points along the relative corrosion-loss graph. The Calumet mine water used in these tests had a free acidity of 410 p.p.m., or 20 p.p.m. less than the same water used in the long-time immersion tests made[82] in 1922. The total acidity was 1,300 p.p.m., or 1,640 p.p.m. less than the average in 1922. These differences should not affect the relative amount of corrosion, but might be expected to cause considerable difference in the conversion factor. Table 11 gives the results obtained in accelerated electrolytic tests on the 12 alloys, with the data from the long-time immersion test compared. The average loss in milligrams per square centimeter per 24 hours is plotted in Figure 14 for each individual alloy as obtained in the two tests. The aim in this series of runs was to determine if the relative losses in the accelerated and long-time tests were the same in the Calumet mine water, since it had been shown that with some exceptions this was the case for Edna No. 2 mine water. As can be seen from Figure 14, the general slope of the two graphs is roughly the same. The relative order of the losses in the accelerated and long-time tests in the Calumet mine water was roughly the same; but the agreement was not so well as in the case of the tests in the Edna No. 2 mine water.

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[82] Selvig, W. A., and Enos, G. M., work cited.

TABLE 11.—*Comparative loss in weight of test pieces in accelerated electrolytic corrosion test and long-time exposure test, for 12 metals and alloys in Calumet mine water.*

Test piece number.[a]	Designation.	Chemical composition, per cent.[b]	Area of test piece, sq. cm.	Weight in grams. Before immersion.	Weight in grams. After immersion.	Loss in weight, gram.	Loss per sq. cm. per 24 hours in accelerated test, milligrams.	Loss per sq. cm. per 24 hours in long-time exposure test,[d] milligrams.
103-a	Rolled rustless steel "B"	Ni 29.60 Si 3.26 Cr 10.73 C low Fe remainder	14.95	14.8131	14.7828	0.0303	6.1	......
103-b			14.17	13.4373	13.4099	0.0274	5.8	......
Average			.....	....	....	......	5.9	0.0427
88-a	Cast aluminum-silicon alloy	Si 3.90 Al 96.10 (by difference)	14.59	10.8441	10.7801	0.0640	13.3	......
88-b			14.17	10.7364	10.6734	0.0630	13.4	......
Average			.....	....	....	......	13.4	0.43
40-a	Rolled monel metal	Ni 65.1 Cu 30.52 Fe 4.2	14.00	13.7534	13.6469	0.1065	22.2	......
40-b			14.12	14.0547	14.9478	0.1069	22.7	......
Average			.....	....	....	......	22.5	0.86
85-a	Cast lead bronze	Cu 74.9 Pb 14.3 Sn 10.5	14.79	47.0409	46.8843	0.1566	31.8	......
85-b			15.43	46.1290	45.9734	0.1556	30.0	......
Average			.....	....	....	......	30.9	0.55
76-a	Cast aluminum bronze	Cu 93.9 Al 6.1 (by difference)	14.68	23.8093	23.6525	0.1568	32.0	......
76-b			14.54	25.2835	25.1195	0.1640	33.8	......
Average			.....	....	....	......	32.9	0.41
79-a	Cast bronze	Cu 89.8 Sn 9.7 Pb 0.5	14.37	42.5970	42.4222	0.1748	36.5	......
79-b			14.65	32.4274	43.2572	0.1702	34.8	......
Average			.....	....	....	......	35.7	0.67
4-a	Cast chromium-iron cupro-nickel	Cu 42.24 Cr 11.89 Ni 35.00 Si 1.50 Fe 9.35	13.95	47.7373	47.5507	0.1866	40.1	......
4-b			13.65	45.0063	44.8169	0.1894	41.6	......
Average			.....	....	....	......	40.9	1.11

[a] *Test piece numbers used are the same as those used in Bulletins 4 and 5, Coal-Mining Investigations, Carnegie Inst. of Technology, 1922-1923.*

[b] *Analyses, unless otherwise noted, were run by C. H. Eldridge and G. B. Dalrymple.*

[c] *Analyses furnished by co-operating company.*

[d] *Average figures are obtained from Bull. 4, Coal-Mining Investigations, Carnegie Inst. of Techonology, 1922.*

TABLE 11.—*Comparative loss in weight of test pieces in accelerated electrolytic corrosion test and long-time exposure test, for 12 metals and alloys in Calumet mine water.—Continued.*

Test piece number.[a]	Designation.	Chemical composition, per cent.[b]	Area of test piece, sq. cm.	Weight in grams.		Loss in weight, gram.	Loss per sq. cm. per 24 hours in accelerated test, milligrams.	Loss per sq. cm. per 24 hours in long-time exposure test,[d] milligrams.
				Before immersion.	After immersion.			
70-a	Cast copper-lead alloy	Cu 53.4	14.12	54.1391	53.9302	0.2089	44.4	......
70-b		Pb 46.4	14.99	51.6938	51.4837	0.2101	42.1	......
Average			.....	....	....	......	43.2	0.72
7-a	Cast tin-lead-nickel silver	Cu 63.52 Zn 11.55 Ni 12.85 Pb 7.49 Sn 4.59	14.49	28.5017	28.2922	0.2095	43.4	......
7-b			14.42	30.2157	30.0020	0.2137	44.5	......
Average			.....	....	....	......	43.9	0.76
115-a	Rolled ingot iron	[c]Fe 99.9	14.09	10.2923	10.0703	0.2220	47.1	......
115-b			13.94	10.2361	10.0303	0.2058	44.3	......
Average			.....	....	....	......	45.7	2.12
28-a	Rolled brass (grain size 0.025 mm.)	Cu 70.80 Zn 28.06 Sn 1.14	13.92	11.0914	10.8682	0.2232	48.1	......
28-b			14.45	11.1627	10.9388	0.2239	46.5	......
Average			.....	....	....	......	47.3	1.09
16-a	Rolled high brass	[c]Cu 66.55	14.31	11.3776	11.1459	0.2317	48.6	......
16-b		Zn 33.45	14.32	11.2314	11.0011	0.2303	48.3	......
Average			.....	....	....	......	48.4	1.42

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[a] *Test piece numbers used are the same as those used in Bulletins 4 and 5, Coal Mining Investigations, Carnegie Inst. of Technology, 1922-1923.*

[b] *Analyses, unless otherwise noted, were run by C. H. Eldridge and G. B. Dalrymple.*

[c] *Analyses furnished by co-operating company.*

[d] *Average figures are obtained from Bull. 4, Coal-Mining Investigations, Carnegie Inst. of Techonology, 1922.*

On a point-by-point examination of the two curves, it will be noted that there is only one wide discrepancy between the results on the materials—that is, the rolled ingot iron. It may be that in the long-time test, colloidal ferrous hydroxide formed on the surface and accelerated the corrosion rate, since it is known that this effect can take place; while in the accelerated test this corrosion product was removed fairly rapidly at the velocity of the rotating test piece. In constructing Figure 14, the actual values for the losses in weight in the long-time exposure test were plotted, but only one-fortieth of the actual values for the accelerated test. The results indicate that the acceleration in the electrolytic test is of the order of 40 times.

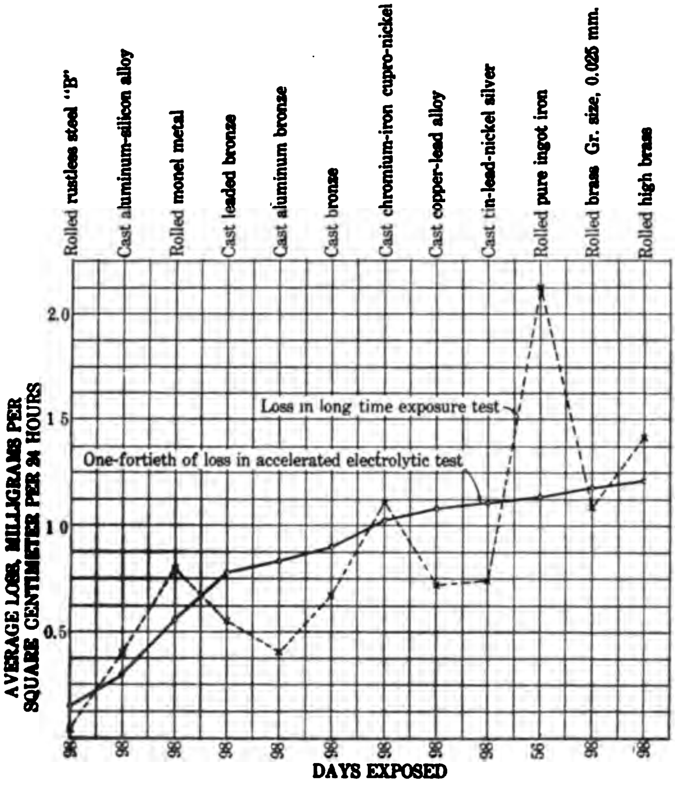

FIGURE 14.—*Comparison of corrosion losses in the accelerated electrolytic test with losses in the long-time immersion test in Calumet mine water.*

From the figures in Table 11 it can be seen that the results obtained in the Calumet mine water as to relative order of losses agree fairly well with the results obtained from the tests in Edna No. 2 mine water.

DATA ON CORROSION IN THE MONTOUR No. 1 MINE WATER.

A set of accelerated electrolytic tests was made in Montour No. 1 mine water, but the results obtained showed no agreement with those of the long-time immersion tests. The great discrepancy found between the relative losses was due to a number of factors and comparison among the results obtained with this mine water and the Edna No. 2 and Calumet mine waters can not be made for the following reasons: First—in the long-time tests in Montour No. 1 mine water, the rate of flow was much different from that in the other two mines, as explained[88] in Bulletin 4; the rate in the Montour mine varied from a negligible to a gentle flow. This differs greatly from the flow regulation in the other two series of tests, and no change was made in the rate of rotation of the pieces in the accelerated test to compensate for this difference. Second—there was marked difference in the free and total acidity of this mine water as used for the long-time immersion tests and as available for the accelerated test. In the former, the water had free acidity of 1,432 p.p.m., and total acidity of 11,360 p.p.m. The water used in the accelerated test had a free acidity for only 410 p.p.m., and total acidity of 1,300 p.p.m. The great variation in these figures precludes the possibility of obtaining check results with the long-time immersion tests, and it was not desired to bring up the acidity of the water artificially.

Because of the variation in the above factors and the great difference in the results obtained, the relative corrosion losses have not been included in this bulletin.

DISCUSSION OF THE ACCELERATED TESTS IN MINE WATER.

Table 12 gives the relative corrosion losses for the accelerated electrolytic and long-time immersion tests in the Edna No. 2 and Calumet mine waters. The alloys are arranged in the order of increasing corrosion loss in the electrolytic test in Edna No. 2 mine water. In Figure 15 the relative losses are plotted for each alloy, thus indicating the relation between the losses for the individual alloys. On examination of the graphs it is seen that they agree closely. Taking the case of curves plotted for corrosion in the Edna No. 2 mine water, point-by-point examination shows that with one-tenth the loss in the accelerated test and actual loss in the long-time test plotted, the two curves have approximately the same shape. In plotting one-tenth the loss in the accelerated test and actual loss in the long-time test for the Calumet mine water it is shown that the two curves are of the same general slope. The relative order of the alloys as to corrosion losses in all four tests is the same with the exceptions already pointed out.

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[88] Selvig, W. A., and Enos, G. M., work cited.

TABLE 12.—*Comparison of the weight losses of test pieces in accelerated electrolytic corrosion test with long-time immersion test in both Edna No. 2 and Calumet mine water. (See Tables 10 and 11.)*

Test piece number.	Designation.	Loss per sq. cm. per 24 hours in Edna No. 2 mine water, milligrams.		Loss per sq. cm. per 24 hours in Calumet mine water, milligrams.	
		Electrolytic test.	Long-time exposure test.	Electrolytic test.	Long-time exposure test.
103-a, 103-b	Rolled rustless steel "B"......	6.15	0.00044	5.9	0.0427
88-a, 88-b	Cast aluminum-silicon alloy...	16.2	2.20	13.4	0.43
85-a, 85-b	Cast lead bronze............	36.0	1.21	30.9	0.55
79-a, 79-b	Cast bronze.................	37.4	2.12	35.7	0.67
70-a, 70-b	Cast copper-lead alloy........	52.8	3.87	43.2	0.72
7-a, 7-b	Cast tin-lead-nickel silver...	55.2	4.24	43.9	0.76
76-a, 76-b	Cast aluminum bronze........	60.2	5.08	32.9	0.41
4-a, 4-b	Cast chromium-iron cupro-nickel.................	64.9	6.58	40.9	1.11
40-a, 40-b	Rolled monel metal...........	68.6	6.68	22.5	0.86
115-a, 115-b	Rolled ingot iron.............	71.55	7.14	45.7	2.12
28-a, 28-b	Rolled brass (Admiralty metal, grain size 0.025 mm.)........	73.9	7.07	47.3	1.09
16-a, 16-b	Rolled high brass............	84.3	7.30	48.4	1.42

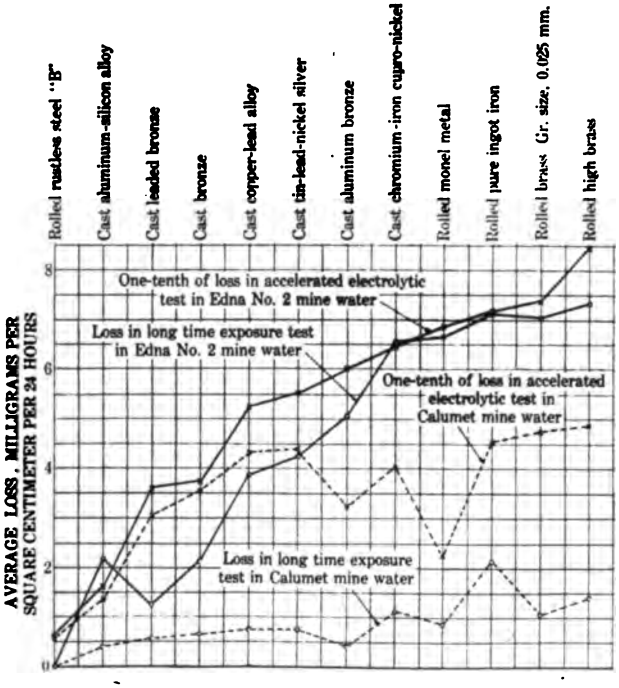

FIGURE 15.—*Comparison of the weight losses of test pieces in accelerated electrolytic corrosion test with long-time immersion test in both Edna No. 2 and Calumet mine waters.*

VALUE OF ACCELERATED ELECTROLYTIC TEST.

From the results of these comparative tests it is evident that the accelerated electrolytic test is of value in examining metals and alloys for relative corrodibility, and, when the various factors affecting corrosion rates are properly accounted for, the results may be correlated with results from the long-time immersion test. With the exceptions pointed out previously, the corrosion losses per unit area per 24 hours, as found in the long-time test and the accelerated electrolytic test for the different metals and alloys, are comparable. The general nature of the corrosion in both tests is the same—that is, as to coatings formed, pitting, and other surface features which are ordinarily observed. While the weight losses in the Montour No. 1 mine water, in the two tests, were not comparable for the reasons previously explained, the general nature of the corrosion in both was similar.

In examining the general corrosion results for the different groups of metals and alloys, as was done in the long-time immersion tests[84], the following observations were made:

1. The alloys of the brass and bronze types were corroded uniformly, the latter being corroded to a much smaller extent than the former. Evidently copper-tin alloys of the bronze type are preferable to copper-zinc alloys for use in mine waters.

2. The cupro-nickel alloys show about the same amount of corrosion as the brasses. In this case also the alloys are corroded uniformly.

3. The nickel-silver alloys were also badly corroded, but here again the corrosion has taken place uniformly. The aluminum alloys have much smaller weight losses than the brasses, bronzes, and nickel-silver group, but they have a tendency to pit badly. This eliminates any possibility for their use in mine water.

4. The rolled rustless steels show the smallest amount of corrosion, and apear to be the most suitable alloys for use in mine water. In this class are included two chromium-nickel-silicon steels

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[84] Selvig, W. A., and Enos, G. M., work cited.

(test specimens 100a and 100b and 103a and 103b) and a high-chromium steel (test specimens 106a and 106b).

5. The conclusions reached as to the behavior of the various metals and alloys in the accelerated electrolytic test using acid mine water as the electrolyte are, in general, about the same as those reached after carrying out the long-time immersion tests[85].

SUMMARY AND CONCLUSIONS.

This bulletin reports results of experiments on the corrosion of metals and alloys in acid mine waters, and the experiments carried out were in continuation of work previously reported in Bulletins 4 and 5. The conclusions to be drawn as the results of the work, together with a brief summary of the investigation, are as follows:

1. It has been shown that there is a great need for an adequate accelerated corrosion test, the results of which can be readily translated into terms of service corrosion.

2. In attempting to develop an accelerated test for corrosion, so-called chemical tests were first carried out, in which oxygen was introduced into the corroding medium (mine water), by bubbling air through the test vessels. It was found that the weight losses were not increased in this method over those obtained in ordinary long-time immersion tests when the results of both were reduced to comparable terms. It is thought, however, that this test may have possibilities of development, provided that a set-up can be arranged which will ensure more intimate contact of oxygen with the test piece.

3. Finding that the chemical test did not yield the desired acceleration, a series of experiments was carried out on an electrolytic corrosion test. Certain work of other investigators was first repeated for checking purposes, and the most suitable conditions for carrying out an accelerated electrolytic test were determined after examining the effects of a number of factors which influence results.

4. Briefly, the method employed for carrying out the accelerated electrolytic test is as follows: A test piece of the metal or alloy to be tested for corrodibility in any electrolyte is prepared of such size and shape that about 14 sq. cm. of surface may be exposed to the action of the corroding medium. A convenient size of

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[85] Selvig, W. A., and Enos, G. M., work cited.

test piece is about 1 cm. in diameter and 8 to 10 cm. long, for cylindrical samples; for square samples, the piece may be about 1 cm. square. The test piece is attached to a rotating spindle of a suitable electrolytic apparatus and made anode; the piece may be conveniently attached to the anode spindle by means of heavy copper wire. The cathode is a platinum wire. About 250 c.c. of the corroding medium is used as the electrolyte in a heavy walled glass vessel. A current of amperage sufficient to yield current density of 0.18 amp. per sq. dcm. of anode area exposed is imposed on the cell. The anode is rotated at convenient speed (such as 140 r.p.m.), and run until a weighable loss is obtained. The time required to yield a weighable loss will also give ordinarily definite indication of the nature of the corrosion—for example, the kind of coating formed and pitting, if any. With mine water as the electrolyte and ordinary bronze as the anode, sufficient loss can be obtained on an eight-hour run.

5. After determining suitable conditions for carrying out the accelerated electrolytic corrosion test, experiments were made in which 42 metals and alloys, which had previously been examined as to corrosion losses in long-time immersion test in acid mine water, were tested by the accelerated test. It was found that the order of losses of the 42 materials in both tests was roughly the same, and roughly the acceleration obtained was about 10 times. This refers to comparison of results in the two tests using Edna No. 2 mine water. In Calumet mine water, the acceleration was about 40 times. Hence, depending upon the materials tested, the corroding medium, the time-period of exposure, and the current density, and taking account of interfering factors such as protective coatings, it is possible to secure a conversion factor by means of which the results of accelerated electrolytic tests can be translated into terms of long-time immersion tests.

6. The accelerated electrolytic corrosion test can be employed to determine the corrosion of metals and alloys in acid mine water and probably some other electrolytes, and the test provides a method for quickly determining the possible life of an alloy. The test provides a method that can be employed by mine operators in determining the suitability of alloys for use in mine waters, and by manufacturers of alloys in developing such for resisting the corrosive action of mine water.

7. If alloys, which are suggested for withstanding certain corroding media—for example, alloys for pump parts in handling acid mine water—require actual long-time test or service test, selection of materials would be an endless task; and the determina-

tion of the most suitable alloys could be arrived at only after years of practical tests and observations. Hence, an accelerated test for corrosion should be of great value to makers and users of alloy materials.

8. The corroded test pieces in this investigation were examined microscopically for general features, and careful observations were made of the nature of coatings formed. Most of the microscopic results and of observations made on coatings have been omitted from this report owing to lack of space.

9. In carrying out future work on this problem, the authors recommend the following: (a) further study of the factors affecting accelerated electrolytic corrosion testing; and (b) correlation of accelerated electrolytic tests on alloys with actual service test data obtained on the life of parts in mine pumps.

APPENDIX.

During the course of the work, a number of metals and alloys were submitted from various sources for test as to resistance to corrosion by acid mine water. Test pieces were prepared and corroded by the accelerated electrolytic test as previously described, using Edna No. 2 mine water for the electrolyte. The time period of exposure was 5 or 6 hours. The results of the tests made on 15 materials are given in Table 13. Comparison of the data may be made with the figures in Table 10. A large number of brass tubes and strips, varying in grain size, were also tested in order to determine the effect of increasing grain size for a given composition upon corrosion losses by the electrolytic test as herein described. While the detailed data for these tests can not be included here, it was found that in general there is very slight increase in corrosion loss with increasing grain size in acid, basic and neutral electrolytes. The results of these tests have been discussed by two of the authors[36] in another place.

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[36] Anderson, R. J., and Enos, G. M., Corrosion of brass as affected by grain size: Paper before the Amer. Inst. of Min. and Met. Eng., New York meeting, Feb., 1924, 11 pp., 6 figures.

TABLE 13.—*Corrosion losses of metals and alloys in accelerated electrolytic test in Edna No. 2 mine water.*

Test piece number.	Designation.	Approximate chemical composition, per cent.	Area, sq. cm.	Weight, in grams. Before immersion.	Weight, in grams. After immersion.	Loss in weight, gram.	Hours tested.	Free acidity, p.p.m. of H_2SO_4.	Loss per sq. cm. per 24 hours, milligrams.	Corrosion characteristics.
				Lead.						
308	Cast pure lead.......	Pb 99.99...	15.00	55.0182	55.0156	0.0026	6	2020	0.69	A "protective" coating, black or grey in color, uniformly over pieces.
309			13.00	48.6343	48.6308	0.0035	6	2020	1.1	
320	Cast chemical lead...	Pb 99.9 ...	14.75	59.5002	59.4976	0.0026	6	2020	0.71	
321			13.92	58.6963	58.6947	0.0016	6	2020	0.46	
				Zinc.						
332	Cast zinc............	Zn 99+ ...	14.20	49.5276	49.1046	0.4230	5	2020	143	All the zinc pieces showed a pronounced tendency toward pitting. They also were covered partly by a grey-black coating.
333			14.18	45.7920	45.3949	0.3971	5	2020	134	
344	Sheet zinc...........	Zn 99+ ...	13.89	14.5282	14.1097	0.4185	6	2020	120	
345			15.19	14.7700	14.2917	0.4783	6	2020	126	
356	Sheet zinc...........	Zn 99+ ...	14.00	10.7378	10.1038	0.6340	6	970	181	
357			14.00	10.6620	9.9931	0.6689	6	970	191	
				Iron and steel.						
396	Cast chromium-alloy steel, hard..........	Cr 18.00... Si 1.00... C 0.65... Mo 0.75... Mn 0.35...	13.73	32.5133	32.4889	0.0244	5	2020	8.5	Very slight action and no precipitates.
397			14.68	35.0335	35.0091	0.0244	5	2020	8.0	
388	Rolled chromium-alloy steel, tough..........	Cr 17.00... Si 0.75... Mn 0.35... C 0.15...	14.00	12.6482	12.6383	0.0099	6	970	2.8	
389			14.00	13.5202	13.5007	0.0195	6	970	5.6	
406	Cast chromium steel..	Cr 13.37... Si 0.87...	15.35	36.5348	36.5290	0.0038	5	2020	1.2	
407			14.18	32.8620	32.8578	0.0042	5	2020	1.4	
380	Rolled chromium steel	Mn 0.11... S 0.007.. P 0.019.. C 0.09...	14.12	12.4502	12.4476	0.0026	6	970	0.74	A slight precipitate on cathode. Solution clear.
381			13.86	14.9988	14.9972	0.0016	6	970	0.46	

NOTE.—*Amperage 0.025; current density, < 0.20 amp. per sq. dcm.*

Iron and steel.—Continued.

414	Copper-bearing steel	....	14.25	14.4803	14.1464	0.3339	6	970	94	Solution cloudy. Brown precipitate on the cathode.
415		....	14.51	12.0129	12.6483	0.3646	6	970	100	

Miscellaneous alloys.

437	Cast nickel-chromium-tungsten alloy........	Ni 60.00... Cr 20.00... W 20.00...	15.98	46.5156	46.4521	0.0635	6	2020	16	A thin green coating, not easily removable, formed on test piece.
422	Cast nickel-chromium-molybdenum-iron alloy	Ni 30.00... C 0.15... Cr 25.00... Mo 5.00... Fe 40.00...	14.27	38.3447	38.2529	0.0918	5	2020	31	Slight precipitate on anode easily removed. Solution and cathode clear.
423			14.03	36.9294	36.8368	0.0926	5	2020	32	
430	Rolled copper-silicon-manganese alloy.....	Si 4.09... Mn 1.60... Cu 94.31...	14.44	8.2103	7.9190	0.2913	6	2020	81	
431			14.29	8.9890	8.6771	0.3119	6	2020	87	
433	Copper-silicon-manganese alloy tubes		19.06	30.9246	30.6647	0.2599	6	2020	55	
434			20.22	30.8561	30.5960	0.2601	6	2020	51	
435	Cast copper-silicon-manganese alloy.....		14.06	37.0097	36.7516	0.2581	6	2020	73	
436			14.57	37.1872	36.9284	0.2588	6	2020	71	

NOTE.—*Amperage 0.025; current density. $<$0.20 amp. per sq. dcm.*

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Bulletin 7

COAL-MINING INVESTIGATIONS

UNDER AUSPICES OF

CARNEGIE INSTITUTE OF TECHNOLOGY,
U. S. BUREAU OF MINES, AND
ADVISORY BOARD OF COAL-MINE OPERATORS AND ENGINEERS.

A STUDY OF THE DESULPHURIZATION OF COKE BY STEAM.

By

ALFRED R. POWELL, Associate Chemist,
Bureau of Mines,

and

JOHN H. THOMPSON, Research Fellow,
Carnegie Institute of Technology.

CARNEGIE INSTITUTE OF TECHNOLOGY,
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1923.

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PREFACE.

Pittsburgh is the greatest industrial center in America, and the heart of the greatest bituminous coal-mining district in the world. It is eminently desirable, therefore, that this city should have an institution which devotes a part of its great facilities to the scientific study of that branch of the industry which is largely responsible for Pittsburgh's development and that of western Pennsylvania.

On May 27, 1919, a number of leading representatives of the coal-mining industry of western Pennsylvania met in conference with the President of Carnegie Institute of Technology with a view of bringing about closer relations between the Institute and the mining interests. It was felt that the advice and co-operation of men in the field were necessary for the training of young men for mining work, and at the conclusion of the meeting the following resolution was adopted:

> That this gathering give its approval and moral and material support to the form of education proposed for the Carnegie Institute of Technology by which students may receive a combined technical, practical, and business training, necessary to fit them for service in the coal mining and allied industries. Further, that the President of the Carnegie Institute of Technology appoint a board of no less than ten men representing the coal mining and allied industries, the United States Bureau of Mines, the State Department of Mines, and the Carnegie Institute of Technology, who will advise and assist in carrying out this program of education and training, particularly in its practical phases to the mining industry and in its co-operation with the United States Bureau of Mines.

Following further the intention of this resolution, the President of the Institute entered into a co-operative agreement on June 1, 1919, with the Director of the U. S. Bureau of Mines whereby full advantage could be taken of the Bureau's laboratories, equipment, and library, as well as of the advice and instruction of its technical staff.

To carry out this new program there was organized during the summer months the Co-operative Mining Courses in the Department of Mining and Metallurgical Engineering, College of Engineering, of the Institute. The course in mining engineering covers four years, and leads to the degree of Bachelor of Science.

PREFACE.

The two-year course in coal mining is planned to prepare men with a certain amount of practical experience for executive positions. The four-weeks intensive summer course in coal mining is designed for miners who aspire to be firebosses and mine foremen.

In a large measure, the new mining, ore-dressing, and coal-washing laboratories at the Institute have been equipped gratuitously by various manufacturers of mining machinery and appliances. Co-operative research through research fellowships is devoted to various problems in coal mining and the utilization of fuels. The Institute selects the fellows, the Bureau of Mines provides the laboratory facilities, and the Advisory Board determines what problems be undertaken, and publishes the reports.

The primary object of this co-operation of the Carnegie Institute of Technology, the U. S. Bureau of Mines, and the Advisory Board of Coal Mine Operators and Engineers is the proper education and training of young men for the mining industry. The ultimate objective is to bring about better conditions and greater efficiency in mining operations. The decrease in reserves of coal and increasing cost of production make it urgently necessary for mine operators and engineers to take advantage of everything which modern science, machinery, and methods can contribute.

EDWARD STEIDLE,
Supervisor, Co-operative Mining Courses,
Carnegie Institute of Technology.

FOREWORD.

The investigation described in this paper was conducted by the Co-operative Mining Courses of the Department of Mining of the Carnegie Institute of Technology and the Pittsburgh Experiment Station of the U. S. Bureau of Mines, in co-operation with the coal-mining industry of western Pennsylvania. Under co-operative agreement, four research fellowships paying $750 per school year of 10 months are supported by the Carnegie Institute. These fellowships are open to properly qualified graduates of universities and technical schools. The research work is carried on in the laboratories of the Bureau of Mines under the direction of a member of the Bureau research staff, and results are published under the joint authorship of the two investigators.

Fellowship holders are required to register at the Institute as graduate students and become candidates for the degree of Master of Science, unless an equivalent degree has been previously earned. The purpose of these fellowships is the solution of problems in mining and utilization of coal.

This bulletin covers one phase of an extended investigation that has been conducted during the past few years—namely, the reduction and removal of sulphur from coal and coke by physical methods of water washing, air cleaning, oil flotation, etc., and chemical methods of gas treatment during the coking process. The great economic importance of discovering new methods of sulphur reduction in making available the higher sulphur coals for coke manufacture justifies the study of all possible methods of desulphurization. In previous papers quoted herein, Mr. Powell has reported the extent of desulphurization obtained in treating the coke with hydrogen. In this bulletin is given the results of steaming the coke. It was found that between 10 and 15 per cent of the total sulphur in the coke is removed by simple steaming at 750° C. With alternate vacuum and pressure treatment the desulphurization is increased to 20 to 25 per cent. However, it is possible that the steaming is much more beneficial than the actual sulphur reduction indicates, since the sulphur removed is almost entirely taken from the surface of the coke, and this surface sulphur may be the part that is easily absorbed by the iron in the blast-furnace. Of the many chemical processes of sulphur reduction thus far tried, steaming results in the greatest removal, and offers the best possibility of receiving practical consideration at some future time when low-sulphur coals have become depleted.

A. C. FIELDNER,
Superintendent and Supervising Fuels Chemist,
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A STUDY OF THE DESULPHURIZATION OF COKE BY STEAM.

By ALFRED R. POWELL *and* JOHN H. THOMPSON.

INTRODUCTION.

Sulphur in metallurgical coke[1] gives rise to many problems and difficulties in furnace operations. Over 1¼ per cent of sulphur is likely to produce an inferior grade of iron, which will, in most cases, be "cold-short." Sulphur will, in addition to causing trouble in the furnace, make it difficult, if not impossible, to work the iron. Any process for removing this deleterious substance from the coke should therefore be of interest and value to both the manufacturer and consumer of coke, if the cost is not prohibitive.

The average annual coke production of the United States during the last 10 years (1912 to 1922) has been 45,404,000 tons. Of this amount, 26,152,000 tons were produced in beehive ovens, and the remainder, 19,252,000 tons, in by-product ovens. (In 1922 the proportions were 22 per cent and 78 per cent, respectively.) Approximately 60 per cent of this total has been used in metallurgical industries, chiefly iron and steel, while the remainder was consumed for domestic or gas-making purposes. The coal used in producing this quantity of coke represents annually, approximately 15 per cent of the total of bituminous coal mined in the United States.

One has only to consider the magnitude of these figures to appreciate the importance of the coke industry to the country in general. Any saving in the production, even though it be relatively small, or any improvement made in the finished product, will amount to large sums. The removal of part—even a small part—of the sulphur from the coke offers such an improvement. In addition to solving one of the principal problems of the steel industry, this removal would create a much greater coal supply from which the coke producer would draw his raw material. Many of the coals of Pennsylvania, West Virginia, and Kentucky are so high in sulphur that their use for the manufacture of metallurgical coke is prohibitive, without preliminary treatment by the present known means of coal cleaning, principally coal-washing, which is not always an effective remedy. Illinois has the greatest potential coal supply of any State in the Union, with the possible exception of Wyoming, which is underlain by immense fields of low-grade subbituminous coal. Nearly all of this Illinois coal will make good coke, if not alone, when used in proper mixtures with other coals; but in most cases the sulphur content is above the limit which can not be reduced by washing in some cases, due to the peculiar combinations of the sulphur compounds in the coal. With these facts in mind, the possibility of removing part of the sulphur should interest the coal mine operator as well as the coke producer; and a new market would be created for the product of the former, which has heretofore only been available to those mining a low-sulphur coal.

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[1] The properties of metallurgical coke, by G. St. J. Perrott and A. C. Fieldner: Paper read before American Society of Testing Materials, June 27, 1923.

Many processes have been tried for the removal of sulphur from coke, including steam; but most of them have not met with any degree of success. The information on desulphurization by steam heretofore available was so meager that the method could neither be approved or disapproved, so this research has been carried on to ascertain its efficacy. The process is not a new idea, but rather an old one which has never been carried to any definite conclusion. In view of this fact and some recent discoveries[2] as to the forms of sulphur in coke, it has been thought well to investigate the utilization of steam more fully.

It has been shown that sulphur exists in coke in the following four forms: ferrous sulphide (FeS), sulphates, free adsorbed sulphur, and sulphur in solid solution with the carbon. As might be expected, the first three of these forms are attacked by the steam to some extent. A study of the removal of each form might therefore be expected to bring forth some interesting information.

The recent rapid growth of the by-product coking industry serves to simplify the matter of a cheap steam supply. Large quantities of heat are now allowed to go to waste, but this heat could be well utilized in the generation of steam. Thus the process of steaming coke could be made comparatively inexpensive.

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[2] Powell, A. R., The forms of sulphur in coke: *Jour.* Amer. Chem. Soc., vol. 45, 1923, pp. 1-15.

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HISTORICAL REVIEW OF THE DESULPHURIZATION OF COKE.

Many processes have been tried for the desulphurization of coke, and these may be classed under the following general headings:

1. Processes involving the passage of gases through the coke.
2. Processes involving the treatment of coke with liquids.
3. Processes involving the addition of compounds to the coal before coking.

A brief historical review of these processes is given herewith. Those methods involving the use of steam will be given in detail, but the scope of this paper will not permit of a complete description of all of the others, and they will be mentioned only as an index to reference.

1. PROCESSES INVOLVING THE PASSAGE OF GASES THROUGH THE COKE.

DESULPHURIZING BY STEAM.

In 1854, Scheerer[3] passed high-pressure steam into an oven before drawing the coke, and claimed a resultant loss of 0.4 per cent in the sulphur content. But no mention was made of the resultant coke loss.

A steam desulphurization process was patented by Claridge and Roper[4] in 1858, in which the coal was coked by a gaseous fuel introduced through a double perforated bottom of the oven. At the end of the coking period, steam was blown in, the supply of heating gas being maintained so as to counteract the cooling action of the steam.

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[3] Scheerer, ———, Verhandlungen des Bergmannischen Vereins zu Freiberg, Berg. u. huttenmannische Zeitung, vol. 13, 1854, p. 239.

[4] Claridge, G., and Roper, R. S., British Patent No. 310, Feb. 18, 1858.

Another process[5] in which steam was used as a desulphurizing agent was patented in 1858. In this the steam was introduced at one side of the oven and withdrawn at the oposite side.

Many special forms of ovens in which steam or some other gas may be used to desulphurize the coke have been designed, and these[6] are but a few of the many patents taken out at that period, which claimed the use of steam to desulphurize coke.

In 1883, Simon and Smith[7] obtained a patent for the use of hydrocarbon vapor and steam to desulphurize coke. The claim was made that the hydrogen resulting from the decomposition of this mixture caused desulphurization to take place.

In another process[8], the steam was generated in the coking mass by the dehydration of some substance added to the coal, such as wet peat, mineral hydrates, or slaked lime.

Woltereck[9] has a process combining the use of air and steam at not over 400°C.[10], by which it is claimed that the sulphur is driven out as the dioxide.

Several investigations have been carried out to determine how much of the sulphur in coke can be removed by passing steam through it at high temperatures, but all of these have been performed with the coke pulverized or in small pieces, and on samples of only a few grams. It is true that many large-scale tests have been run on steaming of coke in gas retorts, but the primary purpose has been to secure a larger gas yield, and therefore as complete decomposition of the coke as possible rather than a selective decomposition of the ferrous sulphide (FeS) in coke.

A small-scale test of the effect of different gases on the sulphur in coke was carried out by Simmersbach and Wolff[11], but the primary purpose of this study was not the desulphurization of coke, but to determine the effect of the constituents of blast-furnace gas on the coke. Nevertheless, the results are applicable, as far as the study of a few grams of pulverized coke will apply, to the general problem of coke desulphurization. The results obtained with steam are shown in Table 1.

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[5] Austin, J., and Armstrong, J., British Patent No. 1226, May 31, 1858.

[6] Cormack, W., British Patent No. 2673, Oct. 28, 1864.

Hunt, B., British Patent No. 2562, Aug. 17, 1868.

[7] Simon, H., and Smith, W., British Patent No. 4871, Oct. 13, 1883.

[8] Williams, J. G., British Patent No. 3520, Feb. 18, 1884.

[9] Woltereck, ——, German Patent No. 261,361, May 2, 1912.

[10] All temperatures, unless otherwise stated, are in degrees Centigrade.

[11] Simmersbach, O., and Wolff, Paul, Das verbalten des koksichwefels in hochofen: *Gluckauf*, vol. 41, 1905, p. 906.

TABLE 1.—*Effect of blast-furnace gases on sulphur in coke.*

Temperature, °C.	Combustion loss, %.	Sulphur as H_2S, %.	Sulphur given off in percentage of total S, %.
500	2.14	0.181	12.84
600	2.94	0.187	13.27
800	16.72	0.519	36.83
900	70.88	0.726	51.52
1000	89.18	0.764	54.34

This coke contained 1.40 per cent of total sulphur. The essential time-factor is not stated. It is probable that some other form of sulphur than hydrogen sulphide (H_2S) came off at the higher temperatures, since it is unlikely that almost half of the sulphur could be retained in the small residue at 1000°. It can be seen, however, that a selective removal of the sulphur took place at the lower temperatures, although it is not large.

In 1871, Philippart[12] gave a complete review of coke desulphurization as known at that time, and this was supplemented by investigations of his own. In the light of present knowledge, his ideas of how the sulphur existed in the coke were entirely erroneous; but the results obtained, as shown by the decrease in total sulphur, are interesting in this connection.

Coke in quantities of 15 to 20 grams, and sized to 2 to 3 millimeters, was placed in a combustion tube and heated to a red heat and 6 grams of water vapor per minute was passed through the coke for periods ranging from 4 to 8 hours. Both coke made in the laboratory and industrial coke were studied, and the results were as follows:

Coke.	Time, hours.	Sulphur.		Ash.	
		Before, %.	After, %.	Before, %.	After, %.
Laboratory No. 1......	4	2.05	1.17	17.95	18.00
Laboratory No. 2......	6	0.80	0.55	6.00	5.90
Industrial............	8	0.62	0.49	9.50	7.50

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[12] Philippart, M. A., Des moyens de dasulfures le coke: *Rev. Univ. des Mines*, vol. 28, 1871, pp. 261-318.

The conclusions drawn were that steam is an excellent desulphurizing agent, and that there was practically no loss of coke as shown by the ash content. The difficulties attending practical utilization of this process are stated to be (1) the heat necessary to keep the process going, and (2) the difficulty of securing penetration to the interior of the large pieces of coke.

A laboratory investigation[13] on the desulphurization of coke by steam was carried out in Russia in 1912. A temperature of 500° was used at first, but scarcely any desulphurization was noted. At 800°, however, there was an abundant evolution of H_2S, and after continuing this for three hours, 44 per cent of the original sulphur content had been eliminated. In the next run the temperature was raised gradually as the desulphurization proceeded. Hydrogen sulphide started coming off at 500°, and the rate of evolution increased with the temperature. At 900°, rapid decomposition of the coke itself took place. The results from three different runs are given as under:

Time, minutes.	Sulphur.	
	Before, %.	After, %.
30	1.98	1.08
45	1.34	0.87
60	1.34	0.82

In view of those results obtained in the laboratory the investigator intended to apply the process to the manufacture of coke. However, as far as known, steaming has not yet been applied to the industrial desulphurization of coke.

DESULPHURIZATION BY AIR.

In 1871, Philippart [14] published the results of some work done by him on the desulphurization of coke by air. These show a fairly high desulphurization in the case of the higher sulphur cokes, without much coke loss. He also investigated the treatment of coke by air under pressure, and obtained a 15 per cent decrease in the total sulphur on a low-sulphur coke.

Philippart describes the process patented by Grandidier for desulphurizing coke by air under pressure. The claim was made by the inventor that complete desulphurization could be secured in less than two hours, because air under pressure penetrated the interior of the large pieces of coke, and at that temperature it was without influence on the carbon of the coke. This process was later investigated by Braconier and Cockerill working separately, who obtained a reduction in total sulphur of 12.5 per cent and 6 per cent, respectively. Both of these investigations were carried on with a low-sulphur coke, and the percentage removed would no doubt have been greater had the original content been greater. Complete desulphurization was not even approached, however, and it was concluded that the process was inefficient.

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[13] Skoredoff, N. E., Desulphurization of coke by steam: *Rev.* de la Soc. Russe de Metall, 1912, pp. 442-444; abstract in *Rev. de Metall*, vol. 10, 1913, pp. 672-3.

[14] Philippart, M. A., work cited.

DESULPHURIZATION BY CHLORINE.

In 1869 a process was patented[15] for the desulphurization of coke by chlorine. This gas was introduced through a perforated bottom of the oven; or some metallic chloride was mixed with the coal and steam introduced during the coking process; or else a mixture of steam and chlorine was passed through the oven.

F. L. Stoner[16] and J. R. Campbell have devised a process in which the coke is treated at the close of the coking period with chlorine, and then is washed to remove the soluble salts.

Fingerland[17] passes chlorine through the hot coke after adding certain catalizers, and claims that the sulphur passes off as sulphur dichloride.

DESULPHURIZATION BY HYDROGEN.

In the investigation of Simmersbach and Wolff[18] on the action of certain gases on the sulphur in coke, the following results were obtained when hydrogen was used.

Table 2.—*Effect of hydrogen on sulphur in coke.*

Temperature, °C.	Combustion loss, %.	Sulphur as H_2S, %.	Sulphur given off in percentage of total S, %.
500	1.56	0.107	7.59
600	1.82	0.324	22.99
800	2.49	0.590	41.87
900	5.01	0.645	45.77
1000	10.06	0.721	51.77

The results of this laboratory test showed fairly effective desulphurization without excessive coke loss.

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[15] Barnes, T., British Patent No. 2233, July 22, 1869.

[16] Stoner, F. L., U. S. Patent No. 887,145, May 12, 1908.

[17] Fingerland, German Patent D. R. P. No. 270,573, June 7, 1913.

[18] Simmersbach, O., and Wolff, Paul, work cited.

In 1920, Powell[19] gave the results of some investigations on the desulphurizing action of hydrogen on coke, in which it was found that nearly all of the sulphur could be removed from coke made in the laboratory during a period of a few hours at a temperature of 1000°. With industrial coke, however, the action was much slower, and only part desulphurization could be secured. Large-scale tests to determine the desulphurizing action of purified coke-oven gas when passed back through the coke showed a reduction of the sulphur from 1.10 to 0.95 per cent. The coke-oven gas contained about 50 per cent of hydrogen. These tests were run over a long period, and the time required for the operation would make impracticable the industrial desulphurization of coke with hydrogen or hydrogen containing gases.

DESULPHURIZING BY CARBON MONOXIDE.

Simmersbach and Wolff[20] obtained the following results on treating coke with carbon monoxide:

TABLE 3.—*Effect of carbon monoxide on sulphur in coke.*

Temperature, °C.	Combustion loss, %.	Residual Sulphur in coke, %.	Sulphur given off in percentage of total S, %.
500	1.49	1.23	12.80
600	1.69	1.17	16.89
800	2.20	0.98	30.80
900	2.35	0.88	37.61
1000	3.06	0.87	38.32

These results show fairly good desulphurizing action of the carbon monoxide when the coke is in a finely divided form. There is also litttle coke loss, as might be expected, due to the reducing atmosphere. The results are not, however, as good as those obtained with hydrogen.

DESULPHURIZING BY CARBON DIOXIDE.

According to Goldschmidt[21], carbon dioxide will not react with ferrous sulphide at temperatures below 1150°, so its desulphurizing effect, if any, must depend upon its reaction with other constituents.

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[19] Powell, A. R., Desulphurizing action of hydrogen on coke: *Jour. Ind. Eng. Chem.*, vol. 12, Nov., 1920, pp. 1077-1081.

[20] Simmersbach, O., and Wolff, Paul, work cited.

[21] Goldschmidt, V. M., Tidskrift, Kem., vol. 17, 1920, pp. 215-218, 221-228.

Simmersbach and Wolff[22], obtained the following figures for this gas in contact with coke:

TABLE 4.—*Effect of carbon dioxide on sulphur in coke.*

Temperature, °C.	Combustion loss, %.	Sulphur as SO_2, %.	Total sulphur given off in percentage total S, %.
500	0.98	0.101	6.47
600	1.08	0.144	8.32
800	3.56	0.175	16.00
900	14.54	0.190	25.46
1000	51.71	0.257	59.24

From these figures it may be seen that carbon dioxide has little selective action on the sulphur, most of the desulphurizing effect being due to the combustion of the coke.

DESULPHURIZING BY NITROGEN.

The following figures were obtained by Simmersbach and Wolff with this gas.

TABLE 5.—*Effect of nitrogen on sulphur in coke.*

Temperature, °C.	Combustion loss, %.	Residual sulphur in coke, %.	Sulphur given off in percentage of total S, %.
500	1.03	1.37	2.41
600	1.43	1.34	4.90
800	2.16	1.33	5.90
900	2.83	1.31	6.97
1000	4.50	1.61	17.35

This shows that nitrogen has a slight desulphurizing effect. Probably no chemical action took place, the nitrogen merely acting as a carrying agent for any sulphur vapor which may have been given off from the sulphur in coke.

DESULPHURIZING BY MEANS OF VACUUM.

In 1905, a patent[23] was granted for the use of vacuum in desulphurizing coke. The coke was to be placed in a vessel in a highly heated state, and vacuum applied by means of a pump, while air was to be admitted at intervals to keep the temperature high. From work done by the Bureau of Mines recently it is doubtful whether such a process could be successful. Vacuum will remove only part of the free adsorbed sulphur, and in ordinary coke this can be produced only by the oxidation of ferrous sulphide. This selective oxidation of ferrous sulphide takes place to best advantage at temperatures around 500°. Coke exposed to air while at the temperature (900 to 1000°) of the coke-oven shows practically no selective oxidation of ferrous sulphide, since the coke itself is oxidized readily at this temperature. Coke kept in a highly heated state will therefore show little oxidation of ferrous sulphide, and consequently have little free sulphur that can be removed by the application of a vacuum.

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[22] Simmersbach, O., and Wolff, Paul, work cited.

[23] Simpson, W. S., British Patent No. 25,574, Dec. 8, 1905.

2. PROCESSES INVOLVING THE TREATMENT OF COKE WITH LIQUIDS.

DESULPHURIZING BY WATER.

The odor of hydrogen sulphide is always noticeable during the quenching of coke, and this has led to a belief that a pronounced desulphurization takes place at this stage. What really happens is that the steam formed acts on the ferrous sulphide, producing hydrogen sulphide. Various authorities have agreed that little desulphurization takes place during quenching.

DESULPHURIZING BY HYDROCHLORIC ACID.

In 1874, Nomaison[24] patented a process utilizing hydrochloric acid to desulphurize the coke. He claimed also that some of the ash was dissolved out by this treatment.

Philippart[25] also investigated the action of hydrochloric acid on coke. By boiling a 1:1 mixture of water and hydrochloric acid with large pieces of coke, and also with the powdered coke, he obtained the following figures:

First run.

	Original coke, %.	Coke after treatment.	
		Pieces, %.	Powder, %.
Sulphur	0.48	0.42	0.35
Ash	12.25	12.10	....

Second run.

	Original coke, %.	Pieces, %.	Powder, %.
Sulphur	0.55	0.45	0.36
Ash	13.20	11.30	....

The cokes used in these tests were low in sulphur, and consequently low in ferrous sulphide, which would tend to give low results. Philippart concluded that hydrochloric acid is not an effective desulphurizing agent.

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[24] de Nomaison, S., British Patent No. 1874, May 29, 1874.

[25] Philippart, M. A., work cited.

3. PROCESSES INVOLVING THE ADDITION OF COMPOUNDS TO THE COAL BEFORE COKING.

DESULPHURIZING BY SALT.

In England, the Calvert process made use of the addition of salt to the coal before coking. The purpose was to form volatile compounds of sulphur and phosphorus with the chlorine of the salt, but later experiments have demonstrated that sulphur is actually increased in the coke by the addition of salt.

The Rowan[26] process also made use of the addition of salt, with subsequent washing of the coke by immersion in water. It is claimed that this process gave good results, but it has never been applied on an industrial scale.

DESULPHURIZING BY LIME AND OTHER ALKALIES.

In 1857, Bleibtreu[27] patented a process for the addition of lime or limestone to the coal before coking.

A later and modified adaption of this idea is the Diehl-Faber process, in which the lime is added in the form of powdered limestone. By following this procedure, no absorption of the sulphur takes place until the limestone decomposes at the full heat of the coking process, and by that time all of the volatile sulphur will have passed off. The lime causes a portion of the coke sulphur to be converted into calcium sulphide, and at the same time the ash constituents are converted into monosilicates. The quantity of limestone added is regulated by the above considerations. This process[28] was investigated in some detail by the U. S. Steel Corporation, which did not adopt the method because it has not been found wholly satisfactory.

The use of sodium carbonate to be added to the coking charge was patented by Spurrier[29]. The beneficial results to be obtained were similar to those supposed to result from the use of lime, except that any sulphates formed were supposed to be washed out of the coke by the quenching process.

DESULPHURIZING BY OXIDIZING AGENTS.

In 1860, Nock[30] patented a process for the desulphurization of coke by the use of a mixture of manganese dioxide, potassium nitrate, or other oxidizing agents, with sodium chloride, to be added to the charge before coking.

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[26] Rowan, T., British Patent No. 327, Jan. 30, 1868.

[27] Bleibtreu, H., British Patent No. 1528, May 30, 1857.

[28] Campbell, J. R., Neutral coke: Orig. Com. 8th Inter. Cong. Appld. Chem., vol. 10, 1912, pp. 73-89.

[29] Spurrier, H., U. S. Patent No. 1,007,153, Oct. 31, 1911.

[30] Nock, George, U. S. Patent No. 28,543, May 29, 1860.

A later patent by Franck[31] claims the addition of manganese dioxide alone to the coking charge.

SCOPE AND GENERAL OUTLINE OF PROCEDURE IN INVESTIGATION.

The chief object of this work was, as previously stated, to determine the efficacy of steam as a desulphurizing agent on coke. Were it possible to grind the coke to a powder and then treat it, the problem would have been greatly simplified. But this could not be done because the blast-furnace operator depends upon the larger pieces of coke to carry the burden in the furnace, and also to supply a porous medium through which the gases may rise. It was necessary, therefore, to investigate the process as applied to the large-size material without altering its structure. With this object in view the work was divided into three major divisions—namely, (1) a study of the fine-size coke; (2) a study of the large-size coke; and (3) a comparative study of the action of steamed and unsteamed coke in the blast-furnace.

FINE-SIZE TESTS.

A study of the fine-size material was first made to determine several facts which would have an important bearing upon the problem in general, and also upon the large-size coke investigation. Four typical cokes were investigated by making a series of temperature runs on each. The temperature was held constant for each run, and runs were made for every 100° from 200° to 800°. The information obtained from these tests, in general, was as follows:

Optimum temperature—Temperature observations were carefully made, and the coke-loss determined throughout the fine-size tests to discover the most ideal temperature for the process.

Sulphur elimination—Analyses were made for all four forms of sulphur, as well as for the total sulphhur, both before and after treatment. These results determined which of the forms were being attacked by the steam, and to what extent.

LARGE-SIZE COKE TESTS.

The information gathered in the fine-size tests was employed wherever possible in testing the large-size material. The most effective temperature was already known, and it was held constant throughout these tests. Runs were made on three of the cokes used in the fine-size work. Ordinary steam flow was first tried on each coke, this being followed by tests employing alternate steam flow with complete vacuum. Steam under pressure, alternating with complete vacuum, was then tried in order to cover all possible conditions. In each case analyses were made for all the forms of sulphur, as well as for the total sulphur. All of these tests were made with an excess steam flow. Tests were then made on one of the cokes to determine the most practical rate of flow.

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[31] Franck, ——, German Patent D. R. P. 274,853, April 12, 1912.

COMPARATIVE STUDY BETWEEN STEAMED AND UNSTEAMED COKE.

As a final conclusion to the work, a study was made on the sulphur of steamed and unsteamed coke while in contact with sponge iron. Conditions at the sponge-iron zone of the blast-furnace were approximated as nearly as possible. Analyses were made of the sponge iron, first in contact with the untreated coke, and then in contact with the treated coke. These last experiments brought to light some interesting facts concerning the behavior of sulphur in the blast-furnace.

THE FORMS OF SULPHUR IN COKE.

There are usually four different forms of sulphur in coke as it is received by the consumer, any one or all of which may be present; but as a rule the coke will be found to contain all four in varying quantities. The amount of each form will be dependent upon the method employed in the manufacture, as well as upon the treatment which the product has received after removal from the ovens. These facts have recently been definitely proved[32] at the Pittsburgh Experiment Station of the Bureau of Mines. The final conclusions of this work were that sulphur existed in the following four forms:

FERROUS SULPHIDE SULPHUR.

The existence of this compound in coke has long been recognized. The chemical changes causing its formation and variation in amount were, however, somewhat in doubt. This compound[33], is the result of the decomposition of the coal pyrite, according to the following reaction: $FeS_2 = FeS + S$. The free sulphur will be converted into hydrogen sulphide in the coke-oven, where the gas is composed of approximately 50 per cent hydrogen. A trace of sulphur remains in the ferrous sulphide in the form of a solid solution known as pyrrhotite or magnetic sulphide of iron. The quantity of sulphur so remaining, however, is so small that it may be neglected, and the pyrite sulphur may be regarded as dividing equally between the residue and the volatile matter of the heated pyrite. The small amount of sulphates which exist in the original coal will be converted to sulphides during the coking process.

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[32] Powell, A. R., The forms of sulphur in coke: *Jour.* Amer. Chem. Soc., vol. 45, 1923, pp. 1-15.

[33] Powell, A. R., Some factors affecting the sulphur content of coke and gas in the carbonization of coal: *Jour. Ind. and Eng. Chem.*, vol. 13, 1921, p. 33.

The percentage of sulphur existing as ferrous sulphide when the coke is "pushed" almost always will be found to be higher than when the coke has cooled. Powell[34] has shown that the quantity of ferrous sulphide is dependent upon the rate and conditions of cooling, and analyses of a typical coke, cooled at different rates, for ferrous sulphide gave the following results:

Sulphur as ferrous sulphide in coke by different treatment.

Condition on Treatment.	Sulphur as FeS, %.
Coke at 700 to 1000° as pushed from the oven	0.34
Coke as it came from the plant	0.20
Coke heated to 850° and quenched quickly	0.24
Coke heated to 850° and quenched after cooling to 500°	0.07
Coke heated to 850° and cooled very quickly	0.01

These results show that one of two things happened during the cooling—namely, either the ferrous sulphide decomposed during cooling, or the ferrous sulphide was absorbed or dissolved during cooling in such a manner that the boiling hydrochloric acid did not decompose it. The first assumption was shown to be the case by analyzing the coke, before heating, and, after heating with slow cooling, for soluble iron and for ferrous sulphide. The figures obtained were as follows:

Treatment.	Soluble iron, %.	Sulphur as sulphate, %.	Sulphur as Fe S. %.
Coke before heating	0.75	0.00	0.20
Coke after heating and slow cooling	0.75	0.03	0.01

Ferrous sulphide, therefore, always exists in coke when pushed, and the amount present when used depends upon the conditions under which it has been cooled.

SULPHATE SULPHUR.

This does not exist in the coke while it is in the oven, but is the result of oxidation, which takes place after removal. In cooling, the ferrous sulphide is decomposed to some extent, forming iron oxide and free sulphur. In the presence of an excess of air, some of this free sulphur will oxidize to form sulphates. Observations on coke which have stood for long periods exposed to the atmosphere have shown a slight increase in the amount of sulphates and a corresponding loss in the ferrous sulphide or free sulphur.

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[34] Powell, A. R., The forms of sulphur in coke: *Jour.* Amer. Chem. Soc., vol. 45, 1923, pp. 1-15.

ADSORBED FREE SULPHUR AND SOLID-SOLUTION SULPHUR.

It is impossible within the scope of this paper to take up all of the details which led to the final designation of these two forms of sulphur, but it has long been known that analyses for ferrous sulphide and sulphates did not account for all the sulphur in the coke. Several years ago, Parr and Powell[35] confirmed the presence of what was supposedly organic sulphur in the coke, but reached no definite conclusion as to its exact nature. In a later publication[36] it was conclusively shown that this sulphur existed in two forms—namely, as free adsorbed sulphur and as a sulphur in solid solution in the carbonaceous mass, or held on the surface in such a form as to exhibit all the properties of a solution. These conclusions were the result of a series of experiments employing the use of the phase[37] rule. By keeping the temperature constant, isotherms were obtained between the vapor pressure of the sulphur in the gaseous phase and the concentration of the sulphur in the carbon-sulphur complex. A study of these isotherms seemed to show that part of the sulphur was present in a free adsorbed state, and still another part as a solid solution; but whether this latter form is a true solid solution or not is still somewhat in doubt. It is certain, however, that if not a true solid solution, at least it is held on the surface in such a manner as to exhibit solid solution properties.

The effects of slow and prolonged heating (conditions similar to coke-oven practice) were also studied, and it was found that the solid-solution form increased and the free adsorbed form decreased correspondingly. This accounts for the absence, or very small amount, of free sulphur in metallurgical coke.

An explanation[38] of this phenomena has been made as follows:

> The absence of absorbed sulphur in coke made by the usual process of slow heating, say over a period of 18 hours, is most reasonably explained as

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[35] Powell, A. R., and Parr, S. W., A study of the forms in which sulphur occurs in coal: University of Ill. Eng. Exp. Station, Bull. 111., 1919, p. 42.

[36] Powell, A. R., The forms of sulphur in coke: *Jour.* Amer. Chem. Soc., vol. 45, 1923, pp. 1-15.

[37] Findlay, Alex., The phase rule, 2nd ed., 1906, 351 pp.

[38] Powell, A. R., The forms of sulphur in coke: *Jour.* Amer. Chem. Soc., vol. 45, 1923, pp. 1-15.

follows: All coals contain organic sulphur in fairly large quantities, and this organic sulphur is uniformly distributed throughout the coal substance. By heating the organic sulphur compounds quickly they would decompose with great rapidity, and the decomposition products would tend to pass out of the mass. The time-factor would be so small that a comparatively small percentage would be retained as a solid solution in the coke carbon, a larger quantity would be held back as adsorbed sulphur at the surface, while the remainder would pass out with the volatile matter. With slow heating rates, however, more opportunity would be given for the solution of the decomposition products, and the sulphur which was adsorbed would have more opportunity to be dissolved in the coke carbon during the long heating time.

In conclusion, then, we may state that the sulphur may be expected to exist in four forms in metallurgical coke—namely, as ferrous sulphide, sulphates, free adsorbed sulphur, and a solid-solution sulphur. A high percentage will be found as ferrous sulphide and solid solution. Small amounts of sulphates and free adsorbed sulphur will be found, but these may be absent entirely especially if the coke has been made by prolonged heating and has been quenched very quickly.

ANALYSIS OF SULPHUR FORMS.

Before taking up the details of the investigation itself it would seem advisable to give at this point the method[39] of analysis employed throughout. This method was evolved during the study of the sulphur forms in coke at the Pittsburgh Experiment Station of the Bureau of Mines, and it has been employed in several investigations, in all of which it has given satisfactory results. There are other methods by which we might obtain the amount of sulphur present in its various forms, but all of these are open to at least one of two objections—namely, inaccuracy or time required. The following method was finally decided upon as combining both of these qualities to the greatest degree, it being reasonably fast and at the same time sufficiently accurate.

METHOD OF ANALYSIS.

Total sulphur.—Any standard method for sulphur may be employed, but the following method has given the greatest satisfaction in this work: A 1-gram sample of the coke, which has been crushed to at least 35-mesh, is thoroughly mixed with four times its own weight of Eschka mixture[40]. The sample is then covered with about an ⅛ inch of the mixture, and ignited for at least one hour at a red heat. The crucible is then removed, the contents carefully stirred, and again ignited for at least 30 minutes. Care should be taken to obtain complete ignition, as the coke is much more difficult to burn to ash than coal or like substances. After cooling, the contents are transferred to a 500-c.c. beaker, and digested with 300 c.c. of 10 per cent hydrochloric acid. The insoluble is filtered off and washed with hot water. The filtrate is then made slightly ammoniacal, and brought to a slightly acid condition with a few drops of hydrochloric acid. The sulphur is then precipitated, while boiling, with 10 c.c. of 10 per cent barium chloride solution. After standing for several hours the precipitate is filtered into an ashless filter, thoroughly washed, and then ignited. The weight of the barium sulphate multiplied by 13.74 will give the percentage of total sulphur in the coke.

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[39] Powell, A. R., The quantitative determination of sulphur forms in coke: To be published in *Jour. Ind. Eng. Chem.*

[40] Eschka mixture: Mg O, 66⅔%; Na_2CO_3, 33⅓%.

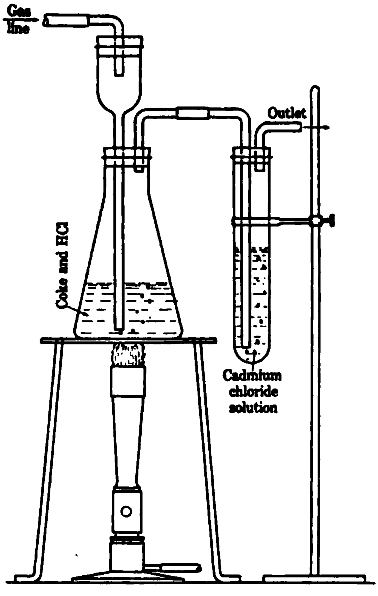

Figure 1.—*Apparatus for determination of sulphur as FeS.*

Sulphur as FeS and sulphates.—A 1-gram sample of the coke (minus 35-mesh) is placed in a 200-c.c. Erlenmeyer flask, and 25 c.c. of water is added. In case of a low-sulphur coke, a 2-gram sample should be used, but for coke with sulphur over 1 per cent, a 1-gram sample will be ample. The flask is then connected to a test-tube containing 10 c.c. of ammoniacal cadmium-chloride solution in such a manner that any gas coming out of the flask will bubble through the solution. (See Figure 1.) Hydrogen is then passed through the flask in order to sweep out any air, and then 25 c.c. of the concentrated hydrochloric acid is added to the flask. The contents are then gently heated until all of the hydrogen sulphide has passed over into the absorption tube. The solution containing the cadmium-sulphide precipitate is then diluted with 300 c.c. of water, acidified with hydrochloric acid and titrated with standard iodine solution. Only the sulphur held as ferrous sulphide will react with the hydrochloric acid to form hydrogen sulphide gas, hence this last titration will represent the sulphur in the form of ferrous sulphide.

The contents of the Erlenmeyer flask are now filtered, the filtrate made slightly ammoniacal, and then brought back to a slightly acid condition with hydrochoric acid. This solution will contain any of the sulphur which might have been held in the coke as sulphates. The sulphur is then precipitated with 10 c.c. of 10 per cent barium chloride solution while boiling. The precipitate thus obtained is treated in the same manner as in the case of total sulphur. The amount of sulphur thus obtained is always very small, and in some cases it may be necessary to allow the solution to stand over night before any precipitate will be noticed. Separation of the iron from the solution before precipitation of the barium sulphate is not necessary.

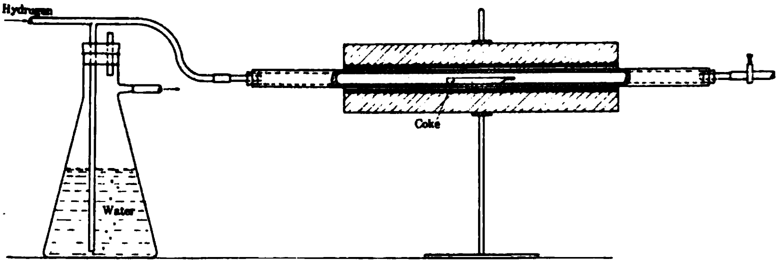

FIGURE 2.—*Reduction apparctus.*

Free sulphur.—A 1-gram sample of the coke (2 grams if the sulphur content is low) is placed in a porcelain boat, which is inserted in a silica tube. This tube is encased in a heating element capable of giving a rapid rise in temperature—from room temperature to 1000° C. in the period of one hour. The tube is then swept free from any air by passing hydrogen through it at a fairly rapid rate. It is then closed at the outlet end, and a positive pressure of hydrogen maintained in the tube throughout the run. This can be accomplished by passing the hydrogen through a T-connection arranged in a flask containing water. (See Figure 2.) The excess hydrogen thus bubbles through the water and escapes. This arrangement also furnishes a positive gage as to the amount of hydrogen flowing, which is a valuable precaution, as explosions of this type are disastrous. The heating current is then turned on and the furnace brought to a full red heat, after which the current is turned off and the system allowed to cool to room temperature, the hydrogen pressure being maintained throughout the operation. The boat is now removed from the tube, and the contents are treated in the same manner as was the sample for determining ferrous sulphide. The sulphur determined in this manner represents the sulphur as ferrous sulphide, sulphate, and any free sulphur which may be present. Since we already know the amount of sulphate sulphur, and also the amount of ferrous sulphide, we can obtain the free sulphur by difference. Occasionally a coke will be found in which the amount of free sulphur will be present in excess of the amount of iron which would be required to convert it to ferrous sulphide, but this will not happen in the case of good metallurgical coke, but may be suspected if the coke is the result of a short heat—say under 8 hours. All of the sulphur of the coal has not had an opportunity to either pass out with the volatile matter or to combine as a solid solution with the carbon. If this condition is suspected, about 0.2 gram of lime should be added to the coke before treating in the reduction furnace. The excess sulphur will be taken up by the lime, and will react under acid just as though it were held by the iron. The difference between these two results will give the amount of sulphur in excess of the available iron (Fe required to form FeS). In case the total free sulphur is all that is desired, a small quantity of lime can be added to all samples, and in this manner complete reduction is certain. However, it is desirable to determine these separately in most cases, because the free sulphur in excess of that which will combine with the iron of the coke may have such a much greater contaminating influence on the iron of the blast-furnace or the cupola.

Solid-solution sulphur.—After these determinations have been made, the ferrous sulphide, the sulphates, free sulphur, and also the total sulphur, will be known. It is then an easy matter to determine the solid-solution sulphur. All of the sulphur in excess of that in the first three forms will be combined with the carbon, and may be determined by subtracting their sum from the total sulphur.

FINE-SIZE TESTS.

In order to make a complete study of the steam effects, it was decided first to test the coke under the most ideal conditious obtainable. This would naturally be in such a size and condition that all of the sulphur compounds, excepting the solid-solution sulphur, would be in contact with the steam. Then by passing a large excess of steam through the mass, the maximum removal of sulphur, as well as many of the fundamental facts concerning its removal, could be obtained. Former work on this subject has shown that coke at minus 35-mesh will yield all of its sulphur, except the solid-solution sulphur, to treatment by either hydrochloric acid or hydrogen. It was therefore decided to crush all of the coke before treatment to pass 35-mesh and remain on 60-mesh. These conditions yielded a coke fine enough to expose the sulphur, and at the same time coarse enough to allow the steam to flow freely through the mass.

The apparatus (See Figure 3) used in this treatment consisted of a specially shaped flask *b*, which was used as a boiler, equipped

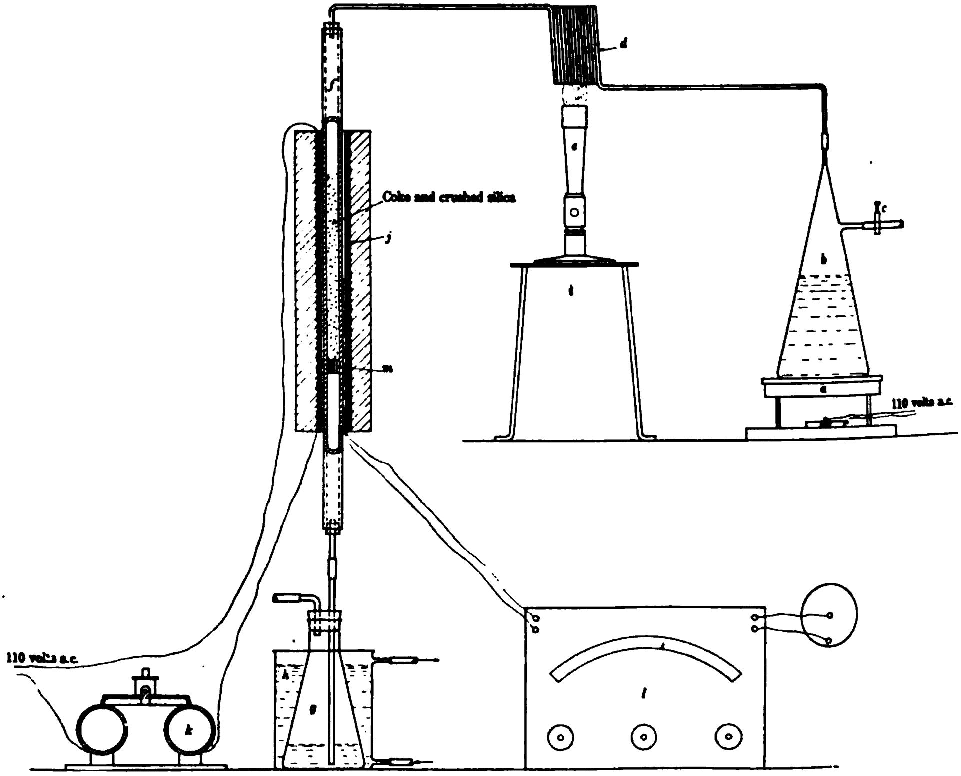

FIGURE 3.—*Steam apparatus for fine-size coke.*

with a release cock *c* to take care of excess steam. It was heated with an electric hot plate *a* so arranged that the temperature could be controlled. By means of the control on the hot plate and the valve *c*, any desired quantity of steam might be passed through the apparatus. The steam was then conducted through a superheater *d*, of coiled brass tubing, heated by means of a large Meeker burner *e*. From the superheater the steam passed down through ⅝-inch silica tube *f*, in which the coke was suspended. An Erlenmeyer flask *g*, containing ammoniacal cadmium chloride, was connected to the lower end of the tube in such a manner that the steam bubbled through the solution and gave up any sulphur it might contain. This flask was kept cool by means of circulating water through a surrounding vessel *h*. The coke contained in the silica tube was heated by means of a circular resistance unit *j*, which was insulated with asbestos. Temperature control was obtained through a sliding rheostat *k*. A Hoskins couple inserted between the silica tube and the heating element, and connected to a potentiometer *l*, gave accurate temperature readings of the coke.

Some difficulty was first encountered in the "packing" of the coke-mass. The slight pressure of steam being maintained caused the finely crushed coke to so pack together as to prevent rapid steam flow. By mixing the coke with crushed silica (plus 20-mesh), and using care in charging, this trouble was overcome. The coke was removed from the silica by passing through a 35-mesh screen, and was thus recovered. A wrapped asbestos plug with small silica tubes leading through it was used to suspend the charge in the tube. (See Figure 3.)

Before treating any of the cokes, a large amount of each, sufficient for all the temperature runs, was crushed and thoroughly mixed. Thus the same material was used during any one set of runs, and analytical work so reduced to a minimum. Runs were then made for every 100° rise in temperature between 200 and 800°. Seven grams of coke was mixed with the crushed silica and charged into the tube as shown in the figure. The temperature desired was obtained in the heating element, the thermocouple removed and the tube put into place. The couple was then replaced, and the steam allowed to flow for 6 hours, at which time practically all action had ceased. Steam flow was maintained at a rate of 10 grams of water as steam per gram of coke per hour. The rate of flow was observed by measuring the condensed water in the Erlenmeyer flask *g*, which had formerly been calibrated.

The collecting flask was removed every 30 minutes, and the cadmium sulphide titrated in the usual manner, an indication of the rate of desulphurization thus being obtained throughout the run. Curves illustrating this point are shown in Figures 4, 6, 8, 10, and 12. At the conclusion of the test the coke was removed

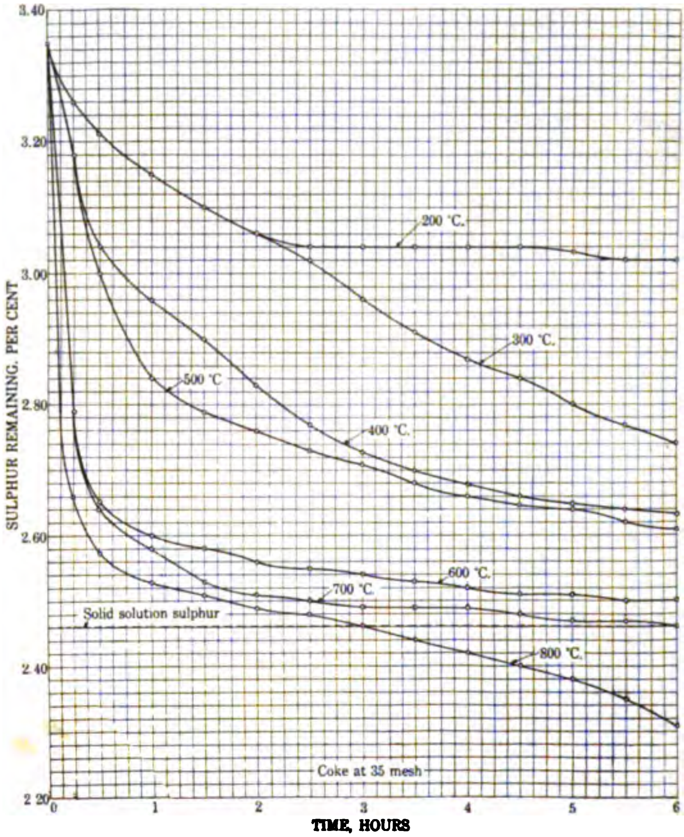

FIGURE 4.—*Rate of sulphur removal at various temperatures from Ohio coke.*

from the tube, free from the silica by screening, and weighed and analyzed for all forms of sulphur. Curves illustrating the removal of each form for each temperature are shown in Figures 5, 7, 9, 11, and 13.

Five different cokes were examined in this manner, and a brief description regarding their origin and prominent characteristics is given herewith:

Coke No. 1.—This was an Ohio coke made from Ohio high-sulphur coal in vertical United Gas Improvement Co. (U. G. I.) retorts at the State University. It was used because of its high-sulphur content. It carried a fairly high percentage of all forms, and a total sulphur of over 3 per cent. In view of this fact it was thought best to examine it first in order to gain an insight into what might be expected from others.

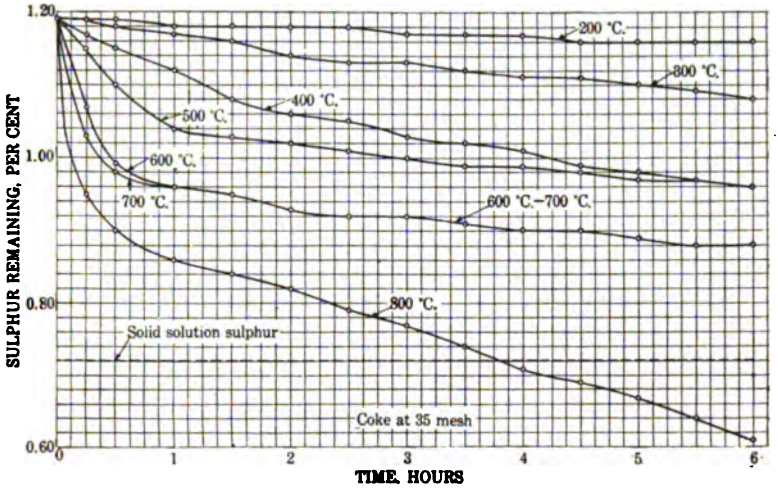

Figure 6.—*Rate of sulphur removal at various temperatures from Illinois coke.*

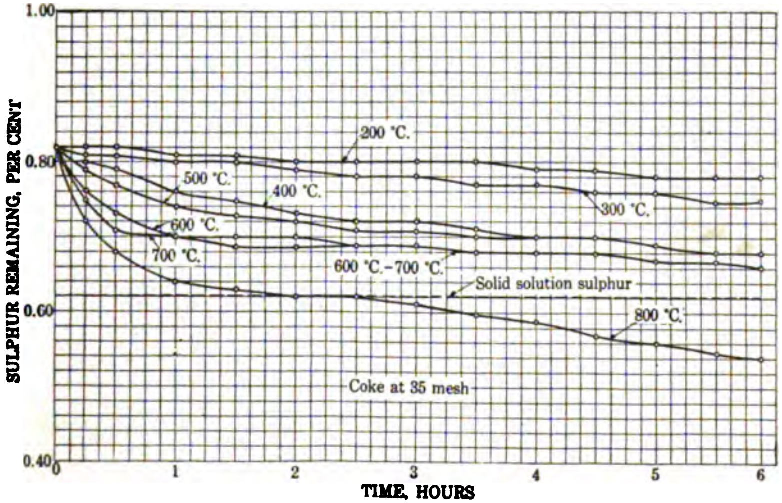

Figure 8.—*Rate of sulphur removal at various temperatures from Pennsylvania metallurgical coke.*

Coke No. 2.—This was a coke made from Illinois coal in Roberts' ovens at Granite City, Illinois. This coke carried sulphur in such quantity that it could be used as metallurgical coke only by special operation of the blast-furnace in order to take care of the sulphur in the slag. Hence, any results obtained on it would give an indication of the practical value of the process.

Coke No. 3.—This was a Pennsylvania coke made in Koppers'

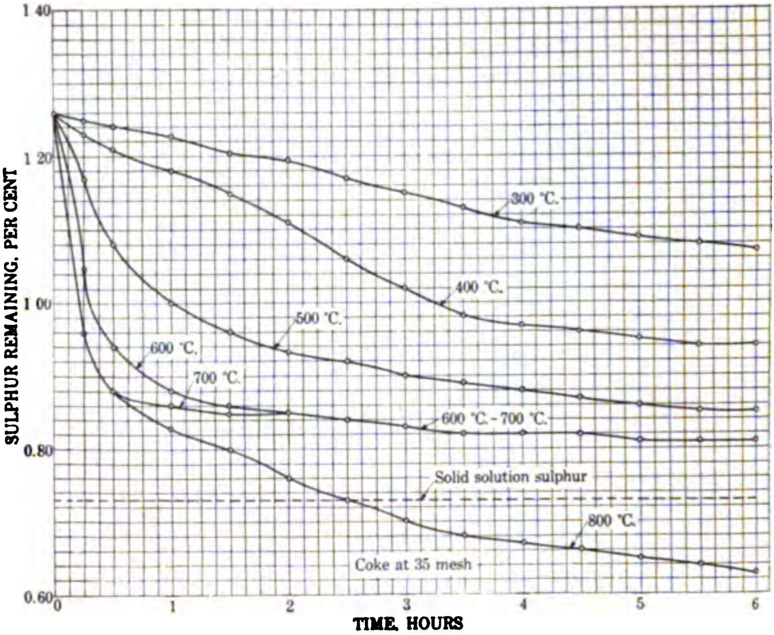

FIGURE 10.—*Rate of sulphur removal at various temperatures from Pennsylvania gas-house coke.*

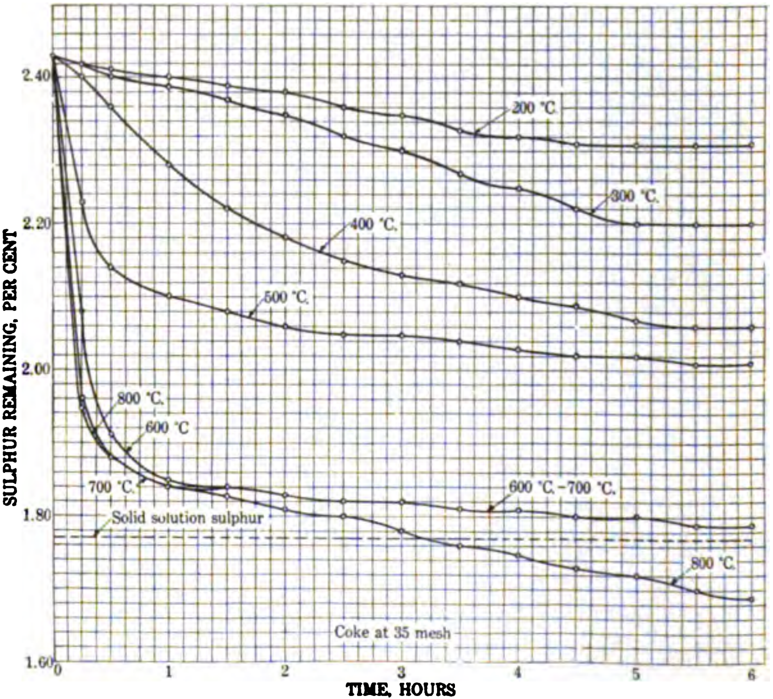

FIGURE 12.—*Rate of sulphur removal at various temperatures from Ohio coke reduced.*

ovens at Clairton, Pa. The opposite extreme of conditions obtaining in coke No. 1 were found in this case. It was a very low-sulphur coke, and a large percentage of the sulphur was present as a solid solution.

Coke No. 4.—This was a gas-house coke made in horizontal U. G. I. retorts by the United Gas Improvement Co., at Philadelphia, Pa. An examination of this product was made in order to gain some idea of what might be expected from cokes made by short-time heating.

Coke No. 5.—This coke was the same as No. 1, except that all of the free sulphur and sulphates were first reduced to ferrous sulphide. Early indications showed that the ferrous sulphide was attacked more readily than the other forms. In view of this fact, the Ohio coke was first reduced to get a high percentage of this form. Thus, only two forms were present in this coke—namely,

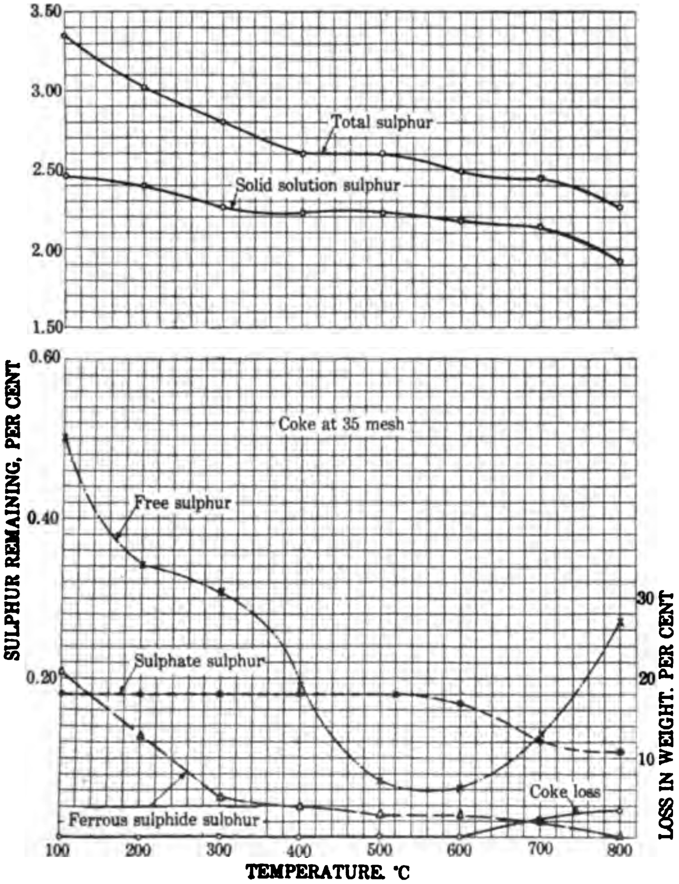

FIGURE 5.—*Sulphur elimination at various temperatures from Ohio coke.*

ferrous sulphide and solid-solution sulphur. Tests were made on this material to determine whether or not the same removal could be accomplished with a large amount of ferrous sulphide present as with a small amount.

SUMMARY OF FINE-SIZE RESULTS.

A study of the curves shown in Figures 5, 7, 9, 11, and 13 will indicate clearly the removal of the various forms of sulphur at different temperatures. These curves were plotted on the basis of the "sulphur remaining after treatment" in order to show the true removal. It will be found that with one or two exceptions the

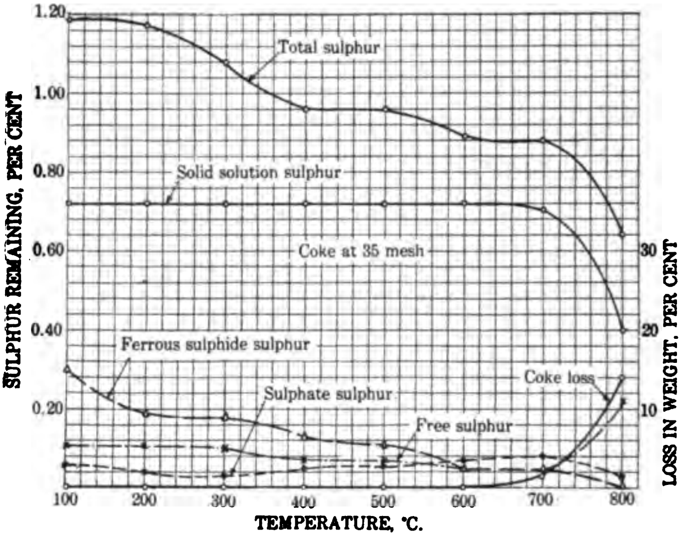

FIGURE 7.—*Sulphur elimination at various temperatures from Illinois coke.*

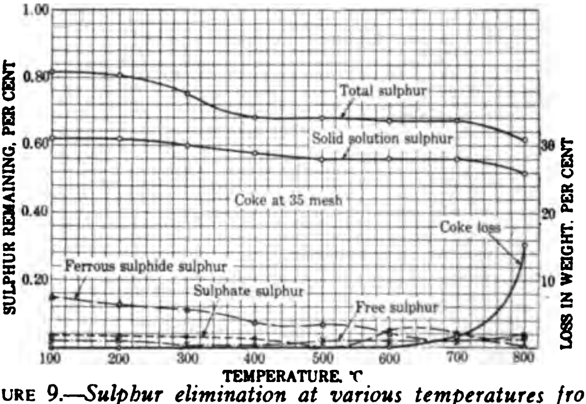

FIGURE 9.—*Sulphur elimination at various temperatures from Pennsylvania metallurgical coke.*

curve for each form exhibits much the same characteristic shape, regardless of the type of coke and the sulphur present.

Ferrous sulphide.—This form was attacked by the steam at all temperatures from 200 to 800°. Any temperature above 500° effected practically a complete removal during the 6-hour period. From 0.01 to 0.02 per cent remained at temperatures up to 700°.

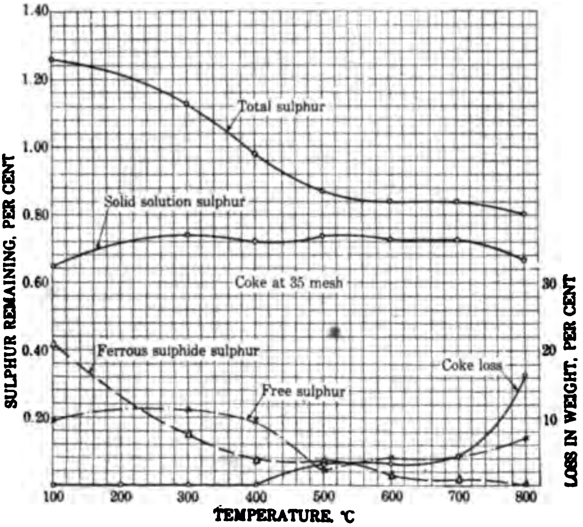

FIGURE 11.—*Sulphur elimination at various temperatures from Pennsylvania gas-house coke.*

This amount seemed to be an inherent part of the coke structure itself, and did not yield until the temperature was sufficiently high to destroy the coke. The "coke-loss" curve plotted on the same graph shows no appreciable change until temperatures over 700° are reached, when it breaks suddenly upward. From this we may conclude that while it is possible to remove this form completely, it is not practical because of the loss to the coke itself.

Free sulphur.—The data on the variations in the free-sulphur content in the coke during steaming are rather confusing, and at times appear to be contradictory. In general, the steaming process removes free sulphur, but not to the same extent that ferrous sulphide is removed. The maximum removal was at 600 degrees.

This removal of the free sulphur can scarcely be explained by the action of the steam as such. However, when steam passes through hot coke, it is decomposed to form some hydrogen, also some carbon dioxide and carbon monoxide. The extent to which the steam is decomposed in this manner depends upon the temperature and period of contact. Since the latter factor is constant for

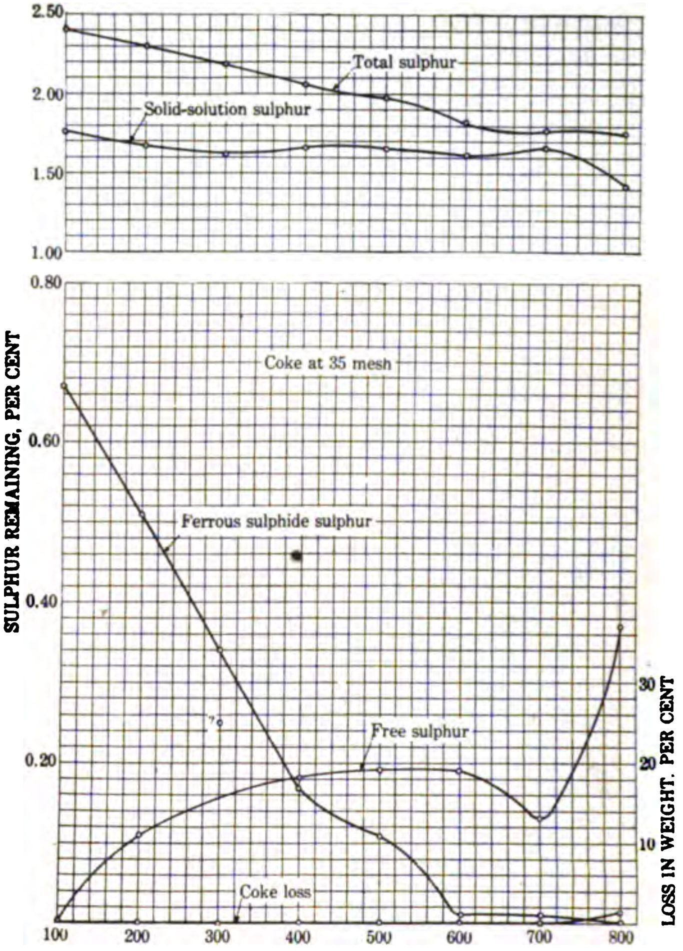

FIGURE 13.—*Sulphur elimination at various temperatures from Obio coke reduced.*

all runs, the temperature of the coke determines how much hydrogen will be produced; and the higher the temperature the greater this amount will be. Hydrogen unites with free sulphur according to the following reversible reactions.

$$H_2 + S \rightleftarrows H_2S.$$

It should be clearly understood that this equation applies to an equilibrium in the vapor phase. The concentration of sulphur in the vapor phase is, however, dependent upon the amount of free sulphur present in the coke, so that the concentration in the vapor phase and the amount of free adsorbed sulphur in the coke are independent. Therefore, the higher the temperature of the coke the more hydrogen will be formed, and more of the free sulphur will be removed as hydrogen sulphide. The character of the curves shows this plainly. At a certain point (about 600°), the free sulphur reaches a minimum, and therefore increases. This is due to two factors, as follows:

In the first place, that portion of the free adsorbed sulphur that has already been removed is that part which will readily enter into chemical combination, while the part remaining in the coke is comparatively inactive. Therefore, despite the increasing concentration of hydrogen as the temperature rises, the available concentration of sulphur falls off at such a rate that the above reaction reaches a comparative equilibrium, and so no more free sulphur is removed. This accounts for the minimum point on the free-sulphur curve.

In the second place, the actual increase in free adsorbed sulphur at, say, 800° as compared to that at 600°, must be explained on the basis that the solid-solution form is converted into free adsorbed sulphur. Several lines of reasoning all lead to this conclusion: The most noticeable phenomenon is the manner in which the free-sulphur curve follows the coke-loss curve from 600 to 800°, showing that as the coke is decomposed sulphur is given out, to be retained in the coke, however, as free adsorbed sulphur. It is interesting, that in spite of the increasing concentration of hydrogen at these higher temperatures, the adsorbed free sulphur in the coke actually increases. This is not inconsistent, however, when it is remembered that steam activates coke or charcoal at these temperatures, thereby greatly increasing its absorbtive capacity.

The results obtained on the free-sulphur content of the reduced Ohio coke, as shown in Figure 13, may be explained from the same fundamental principle. In this case the adsorbed free sulphur in the coke increases up to 600° and falls off at 700°, followed by a marked increase at 800°. This coke contained no free sulphur before steaming. Therefore we should expect the equation

$$H_2 + S \rightleftarrows H_2S$$

to proceed in the opposite direction until sufficient free sulphur had been formed to produce equilibrium. A large quantity of hydrogen sulphide is given off by the decomposition of the ferrous sulphide, and this decomposes to give off free sulphur until equilibrium is reached.

In determining the free sulphur in Pennsylvania gas-house coke, an interesting case was discovered: After several failures to check the free-sulphur content of this coke, an investigation was made with a view to discovering the trouble. It was found that it contained free sulphur in excess of the iron required to unite with it to form FeS. The addition of lime (CaO) to the sample before reduction with hydrogen caused the free-sulphur content to increase markedly. No difficulty in checking results was noticed when lime had been previously mixed with the coke. This phenomenon is probably the result of short-time heating. Gas-house practice requires that the coal be heated as rapidly as possible, and the coking period rarely exceeds 8 hours. Some of the sulphur which would have either passed out with the volatile matter or formed a solid solution with the carbon is left in a free state. This is a pernicious form, probably yielding itself readily to the iron in the furnace. In foundry and cupola practice, where these cokes are sometimes used, this condition might easily account for some of the "high-sulphur" troubles. Cases have recently been called to the authors' attention in which cokes with apparently the same total sulphur and treated in the same manner, produced a finished iron of widely differing sulphur contents. Recent investigations show beyond a doubt that the form in which the sulphur occurs in the coke has a decided influence on the amount of sulphur absorbed by the iron at high temperatures.

Sulphate sulphur.—With one exception, all of the cokes examined carried so little sulphur as sulphates that they are of no value as an index on the removal of this form. In the case of the Ohio coke (Figure 5), there was a sufficient amount present, however, to furnish some idea of what might be expected from sulphur in this form. The amount of sulphate sulphur was found to remain practically unchanged for all temperatures up to 700°. This would seem to indicate that a neutral or slightly oxidizing atmosphere existed up to this point. Such conditions might have been expected from observations already made as to the relative amounts of free sulphur present at these temperatures. At 700° sudden decrease in the amount of sulphate was noticed, and at 800° this condition was found to be even more pronounced. The maximum removal (about 50 per cent) of this form was found to take place at 800°. In the case of the other cokes it will be noticed that the sulphate varied somewhat with an increase in tempurature. This variation is slight (0.01 or 0.02 per cent), and since the original content was in no instance over 0.06 per cent, errors in the analyses and sampling may readily explain this fluctuation.

Solid-solution sulphur—This form was practically unaffected at all temperatures up to 700°. In the case of the Ohio coke

(Figure 5) it was found to decrease slightly with an increase in temperature. This coke was an experimental product and poorly made. The solid-solution sulphur was therefore probably not held in the carbon as tenaciously as in the case of the regular 18-hour metallurgical product. The Pennsylvania coke (Figure 9) also shows a slight variation in this form. This may be accounted for when we consider the method of analysis previously described. The solid-solution form was found by difference after all other forms had been determined. Any slight errors in the determination of the first three will show in the solid-solution determination.

At 700° the solid-solution curve for each coke begins to decrease suddenly, which is explained by the coke-loss curve. Above 700° the coke is attacked by the steam, and the sulphur of the carbon-sulphur complex is then partly removed.

Total sulphur.—The total sulphur in each case was found to decrease with an increase in temperature, reaching a maximum removal at 800°. In the case of the Illinois coke, the removal at this temperature was almost 50 per cent. These figures are of interest to the investigation, but of no value as regards the practical application of the process. At temperatures above 700° the coke-loss becomes so great as to render the corresponding increased removal impractical; 700° seems to be the optimum temperature for the process. At this point practically no coke-loss was noticed, and the removal of the sulphur was fairly appreciable. With the exception of the Pennsylvania metallurgical coke, the total sulphur removed at this temperature was about 25 per cent. Could these figures be duplicated on the large-size material, the process would undoubtedly be of practical value.

As previously explained, samples were taken every 30 minutes throughout each run, the data thus gathered making possible the plotting of "rate of desulphurization" curves for each temperature. These curves will be found for each coke in Figures 4, 6, 8, 10, and 12. They were plotted on the basis of the "sulphur remaining," and show graphically the amount of total sulphur removed during any time-interval. Their chief value to the study is found in the fact that they show definitely the time required to effect efficient desulphurization.

Certain general characteristics will be noticed for all cokes: At the lower temperatures—namely, 200, 300, and 400°—the curves have a gradual slope, becoming less pronounced after the first hour. This indicates that the sulphur removal was greatest during the first hour, and that considerable sulphur was removed during all time-intervals. The curves for 500°, 600°, 700°, and 800° are increasingly steeper during the first hour, and seem to flatten out from there on. In other words, the greater proportion of the sulphur was removed during the first hour. In every coke examined the curves for 400 and 500°, and those for 600 and 700°, tend to meet, and in some cases actually do so. This indicates that for steaming periods as long as 5 or 6 hours, 400° is just as effective a temperature as 500°. The 600° and 700° curves exhibit the same phenomena.

Since 700° was found to be the optimum temperature, a detailed study of this curve will give some idea of the amount of time required for desulphurization. It will be noticed that in every case this curve has a very steep slope at first, and then gradually flattens out, until, after 2 hours, it becomes almost a horizontal line. It is safe, therefore, to conclude that for fine-size material very little will be gained by steaming the coke for more than 2 hours. The large-size material probably will require a longer time, but in all probability this time should not exceed 4 hours. Subsequent work on large-size material has shown this to be the case.

The percentage of sulphur as a solid solution is shown as a straight horizontal line. It will be noticed that the 700° curve does not cross this line for any of the cokes examined. The 800° curve, however, cuts through this line in all cases. This might be expected if it is recalled that at 800° the coke was attacked by the steam, and some of the solid-solution sulphur removed. It does not follow, however, that steaming at 800° for the time shown between zero and this point of crossing would remove all other forms, and leave the solid-solution sulphur unaffected. Evidence to the contrary is found in the fact that even after 6 hours treatment at 800° some of the sulphate and some of the free sulphur was still present. The coke was probably being attacked throughout the entire run, and some of the sulphur in all its forms was being removed at all times. The purpose of showing the solid-solution line was to illustrate the point that temperatures of 800° or more effect the removal of some of this form of sulphur. This can not take place without a subsequent coke loss, and hence temperatures in excess of 700° are impractical.

CONCLUSIONS REGARDING TESTS ON FINE COKE.

The results from the fine-size tests provide the following general conclusions:

1. Steam does act as a desulphurizing agent on coke, effecting a removal of 25 to 30 per cent of the total sulphur at 700° on the fine-size material.

2. A greater removal can be effected by treatment at temperatures higher than 700°, but this removal is accompanied by a corresponding coke-loss; hence 700° may be considered the optimum temperature of the process. In the work on large-size coke, a temperature of 750° was used with no appreciable loss; temperatures above this point however, resulted in a prohibitive coke loss.

3. At 700°, all forms of sulphur, except the solid solution, are attacked by the steam. Ferrous-sulphide sulphur is practically all removed. Free sulphur is removed to a large extent, in some cases as much as 75 per cent. Sulphate sulphur is removed at 700°, but not as readily as the other two forms. Solid-solution sulphur is practically unaffected, and the removal of this form can only be accomplished by destroying the coke itself.

4. The most effective period of treatment for the fine-size material is about 2 hours, which period will probably be somewhat increased for large-size material.

LARGE-SIZE COKE TESTS.

SAMPLING.

Before going into the details of the large-size work it would seem advisable to describe the method of sampling employed. The necessity of treating the large piece of coke without altering its structure made true sampling impossible. It has been found from previous tests that the sulphur content of large pieces of coke, even though they have been taken from the same batch, may vary appreciably; but by cutting the sample from the piece itself this difficulty could be overcome to some extent. Three different methods have been tried, the following being selected as being the most nearly accurate:

Two 1-inch slices were cut from a piece, the slices being made at right angles to its longest dimension. Pieces averaging about 3 inches in diamenter and 7 inches in length were used for all the work. A 1-inch slice (*a-a* of Figure 14) was taken one-third the distance from each end. This slicing was accomplished by a thin elastic carborundum wheel rotating at a speed of 1200 r. p. m., a 3-inch piece of the most refractory coke being cut in this manner in a few minutes.

The two 1-inch slices *a-a* were used as the sample "before treatment," and the three remaining chunks *b-b-b* were treated. These were then pulverized to supply the sample "after treatment." It might be suspected that in treating the large piece with its length thus reduced, conditions would not be similar to those obtained by treating the original piece. This may be true, but the difference, if any, will be slight. The pieces for treatment were always so cut that their length exceeded their diameters. The maximum penetration of the steam into the interior will no doubt take place along the shortest dimension. Thus, by keeping the diameter of the cut pieces shorter than their respective lengths, conditions will be almost identical to treating the entire piece.

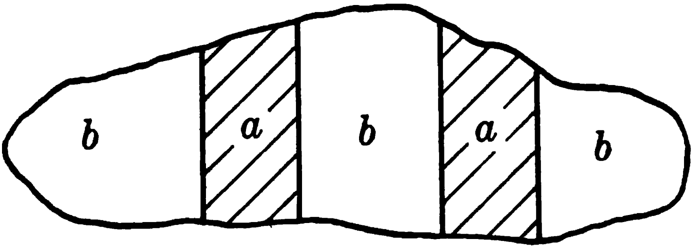

FIGURE 14.—*Method of sampling coke.*

In order to prove that this method of sampling is applicable, all four of the cokes to be treated were sampled. Analyses for all forms of sulphur were then made on the sample, also on the remaining portion; and these two sets of results should check if the sample thus taken were a true sample. The results obtained are given in Table 6 following:

TABLE 6.—*Results of sampling tests (per cent).*

Sulphur as	Ohio experimental coke.		Illinois metallurgical coke.		Pennsylvania metallurgical coke.		Pennsylvania gas-house coke.	
	Original.	Sample.	Original.	Sample.	Original.	Sample.	Original.	Sample.
Ferrous sulphide..	0.39	0.37	0.22	0.23	0.12	0.13	0.15	0.13
Sulphates........	0.13	0.14	0.00	0.00	0.00	0.00	0.00	0.00
Free sulphur.....	0.98	1.17	0.04	0.03	0.03	0.00	0.58	0.57
Solid solution.....	1.78	2.02	0.70	0.75	0.55	0.61	0.18	0.17
Total sulphur...	3.28	3.70	0.96	1.01	0.70	0.74	0.91	0.87

In all four cokes the ferrous-sulphide sulphur and the sulphate sulphur check closely for the respective cokes. With the exception of the Ohio coke, the free-sulphur values also yielded close checks.

The sulphur of this coke exists irregularly throughout the piece, making true sampling almost impossible. It was therefore decided not to treat large sizes of this coke, as the results could not be relied upon.

It will be noticed that the solid-solution sulphur varied appreciably in all cases, but many previous tests made by the Bureau of Mines verify these results. Analyses on different pieces from the same batch, as well as different portions of the same piece, invariably point to similar phenomena. The sulphur as ferrous sulphide, sulphates, and free sulphur does not vary appreciably, but the solid solution sulphur may vary as much as 50 per cent. Since this form is not affected by the steam, this variation is not important. The actual sulphur removed is shown by the difference between the sum of the first three forms "before treatment" and "after treatment." Since these forms are determined collectively by analysis on a reduced sample, there is little chance for error as regards the actual sulphur removed.

However, in order to obtain comparative results on the total sulphur, it was necessary to re-calculate on the basis of the true solid-solution sulphur. Since the amount of coke treated was about five times as great as the sample (not treated), it seemed likely that the solid-solution figure resulting from the treated portion was more nearly correct than that for the sample. The amount found in the portion after treatment was therefore considered as existing in the sample itself. Since the other forms were already known for both the treated and untreated portion, by adding this constant figure to their sum, the total sulphur figures would actually show the sulphur removed. A typical analysis and the calculated values is given herewith:

Comparison of sulphur by analysis and calculated.

Sulphur as.	Before treatment, %.	After treatment, %.	Before treatment—values calculated on the true solid-solution sulphur basis, %.
Ferrous sulphide	0.29	0.14	0.29
Sulphates	0.00	0.00	0.00
Free sulphur	0.06	0.01	0.06
Solid solution	0.66	0.81	0.81
Total sulphur	1.01	0.96	1.16

It will be noticed that the ferrous-sulphide sulphur and the free sulphur show a combined reduction of 0.20 per cent. This removal was checked by measuring the hydrogen sulphide evolved. The solid-solution sulphur, obtained by subtracting the first three forms from the total, shows an increase of 0.15 per cent, which, of course, is impossible, and is caused by the variation of the solid-solution sulphur through the chunk. By assuming the sample "after treatment" as being correct, the total sulphur figures are made to show the true removal.

APPARATUS.

The apparatus used for the work consisted essentially of a retort *a* (See Figures 15 and 16), a condenser *b*, a vacuum-pump *c*, a rheostat *d*, a potentiometer *e*, and an ammeter *f*. The retort was constructed of ¼-inch Shelby cold-drawn tubing, and it was designed to resist 100-lb. pressure at temperature as high as 1000° C. Heat was supplied to the retort by means of an electric-resistance

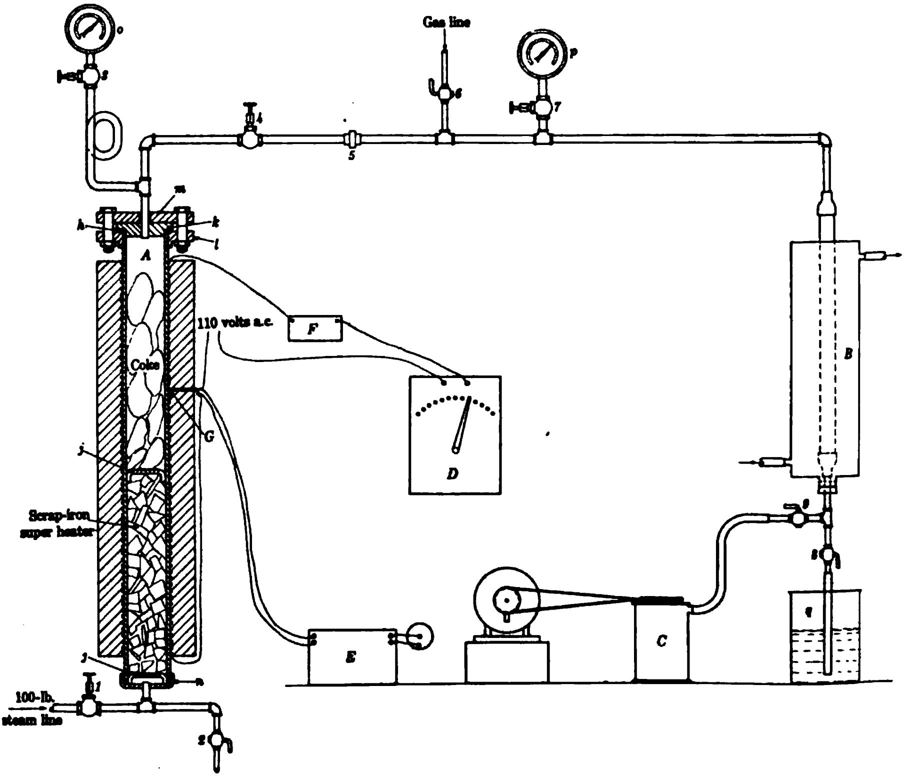

FIGURE 15.—*Diagram of steaming apparatus for large-size coke.*

element wound on the tube itself, 100 feet of ¼-inch nichrome ribbon being used in the winding. A current of from 30 to 60 amperes at 110 volts was required to heat the retort to 800°. Heat insulation was obtained by wrapping the retort with a 2-inch layer of Johns-Manville magnesia pipe covering. Provision was made for accurate temperature readings by inserting the thermocouple *g* into a silica tube, as shown in the figure.

The bottom cap *n* was shrunk onto the tube after first being drilled to fit the ¼-inch steam line. In order to obtain a steam-tight joint at the top, and at the same time furnish a removable fitting for charging, a specially designed apparatus was made. This consisted of a 7-inch steel collar *l*, threaded to the tube so as to come just flush with it. The special piece *k* was so shaped as to allow the lower part just to enter the tube. The upper part rested on the copper gasket *h*, which served as a fitting between the tube and the piece itself. A blind flange *m*, drilled at the center to allow entrance for the steam line, rested upon the piece *k*. Both this

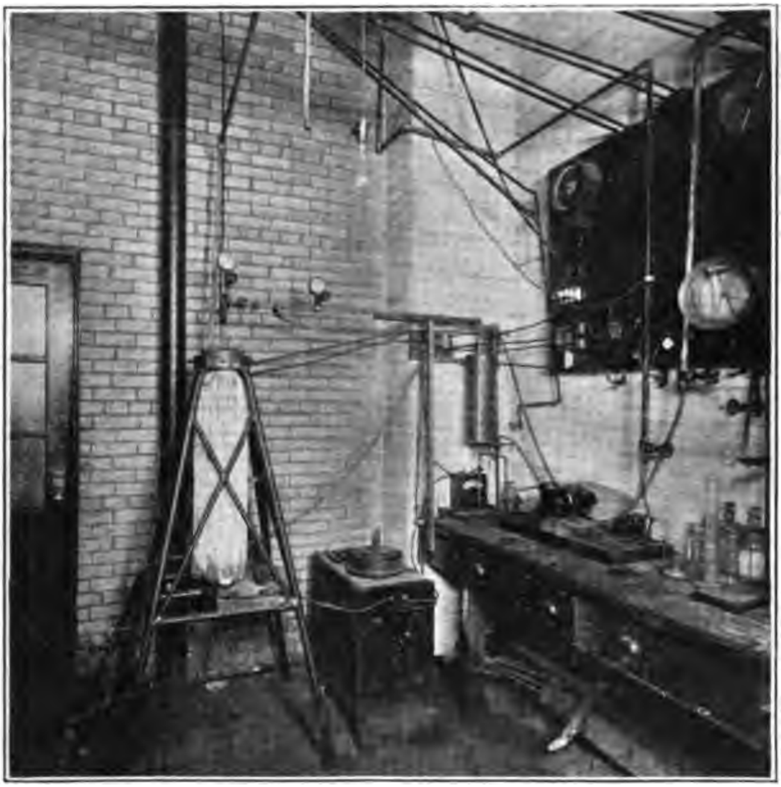

FIGURE 16.—*View of steaming apparatus for large-size coke.*

flange and the collar were drilled to take six ¾-inch bolts. Thus, by drawing up on the bolts, the piece *k*, and the tube were pulled together against the copper gasket. This fitting gave a steam-tight joint for all pressures used.

The lower half of the retort was filled with scrap iron, which was supported at the bottom by means of an inverted cap, drilled with numerous small holes so as to disperse the steam. A similar cap was placed on top of the scrap iron, and served as a support for the coke charge. Since the temperature of the retort never dropped below 700°, no steam could reach the coke without first being thoroughly preheated by the red-hot iron.

The condenser *b* consisted of a copper cylinder 2 feet long and 6 inches in diameter. Taps at the top and bottom provided for the circulation of cold water. The steam line was conducted through this shell. In order to increase the capacity of the condenser it was necessary to enlarge the steam line at this point from ¼ to 1 inch.

The vacuum-pump, potentiometer, rheostat, and ammeter are all standard equipment, and need not be described. The gage *o* furnished pressure readings, and the gage *p* indicated the degree of vacuum obtained. The calibrated flask *q* received the condensed steam, and thus a measure of the amount of steam used could be made. The pipe fittings No. 1 to 9 and their functions can be best described under "Method of Procedure," following.

METHOD OF PROCEDURE.

Three different methods of treatment were tried on each coke—namely, (1) natural steam flow at a constant rate; (2) natural steam flow alternating with complete vacuum; and (3) steam under 100-lb. pressure alternating with complete vacuum.

Natural steam flow.—Pieces of each coke were first sampled as described, and charged into the retort. After the top fitting *k* had been made tight, and the union *5* connected, current was turned on. When the retort reached a temperature of 750°, the valve *l* on the steam line was opened. This valve was so set as to give a uniform flow of steam at the rate of 10 c.c. of water as steam per gram of coke per hour. Steam was allowed to flow through the retort, and was condensed in *b*. It then flowed into a measured volume of sodium hydroxide solution *c*, which reacted with the hydrogen sulphide and thus was obtained by titration a measure of the sulphur evolved. Samples of the condensed steam were thus taken every 30 minutes. These results not only furnished a check on the analysis of the coke before and after treatment, but also gave an indication of the rate at which desulphurization was taking place. The runs were continued until a 30-minute sample showed less than 0.01 per cent of sulphur reduction in the coke. The average period required to reach this limit was about 4 hours.

Natural steam flow alternating with vacuum—In making these tests the coke was charged as previously described. After the desired temperature had been reached, steam was allowed to flow through for a few minutes until the temperature became constant at 750°. Complete evacuation of the apparatus was made every 5 minutes thereafter throughout the run, approximately one minute being required to do this. During the remainder of the 5-minute period, steam was allowed to flow at a rate of 10 c.c. of water as steam per gram of coke per hour. The vacuum obtained varied from 1 to 4 inches of mercury pressure.

Evacuation was accomplished as follows: Steam was shut off at the valve *1*, the system was drained by opening drain cock 2, which was then closed, and city gas was run through the condenser by opening cock *6*. This precaution was taken so as to avoid the entrance of water into the vacuum-pump. Cock *8* was then closed, and *9* was opened, after which the pump was turned on. After the required degree of vacuum had been obtained, the retort was cut off from the condenser by closing valve *4*. Steam was turned on at *1*, and at the same time the vacuum was released in the condenser by opening *6* for a moment. As soon as pressure began to show on the steam gage, valve *4* and cock *8* were opened, and steam was then allowed to flow for the remainder of the five minutes, and the cycle repeated.

Steam under pressure alternating with vacuum.—The procedure in this case was essentially the same as with the previous test. The cycle of operation was identical, except that instead of opening *4* at the first indication of pressure, it was left closed until a pressure of 100 pounds was obtained. It was then slowly opened, and the steam under pressure released into the condenser. Steam was allowed to flow naturally when not applying vacuum or pressure.

In all three cases the condensed steam was allowed to flow into a solution of sodium hydroxide. Samples of this solution were taken every 30 minutes and titrated, furnishing a check on the sulphur removal, as well as an indication of the rate of desulphurization.

SUMMARY OF RESULTS FROM LARGE-SIZE COKE.

The results obtained on the large-size coke tests are summarized in Tables 7, 8, and 9, which show the reduction of each form of sulphur for all three of the methods used.

TABLE 7.—*Sulphur removal from large-size Illinois metallurgical coke (per cent).*

Sulphur as	Natural steam flow.[a]		Vacuum alternating with natural steam flow.		Vacuum alternating with steam under pressure.	
	Before treatment.	After treatment.[b]	Before treatment.	After treatment.	Before treatment.	After treatment.
Ferrous sulphide.........	0.46	0.32	0.55	0.40	0.35	0.23
Sulphates...............	0.03	0.01	0.00	0.00	0.01	0.01
Free sulphur............	0.13	0.15	0.08	0.08	0.19	0.09
Solid-solution sulphur.....	0.70	0.70	0.54	0.54	0.61	0.61
Total sulphur..........	1.32	1.18	1.17	1.02	1.16	0.94

[a] *Natural steam flow, 10 cc. water as steam per gram of coke per hour.*
[b] *Time of treatment, 4 hours.*

TABLE 8.—*Sulphur removal from large-size Pennsylvania metallurgical coke (per cent).*

Sulphur as	Natural steam flow.[a]		Vacuum alternating with natural steam flow.		Vacuum alternating with steam under pressure.	
	Before treatment.	After treatment.[b]	Before treatment.	After treatment.	Before treatment.	After treatment.
Ferrous sulphide.........	0.23	0.16	0.28	0.18	0.22	0.10
Sulphates...............	0.00	0.00	0.00	0.00	0.00	0.00
Free sulphur............	0.06	0.01	0.05	0.00	0.09	0.00
Solid-solution sulphur.....	0.66	0.66	0.76	0.76	0.78	0.78
Total sulphur..........	0.95	0.83	1.09	0.94	1.09	0.88

[a] *Natural steam flow, 10 cc. water as steam per gram of coke per hour.*
[b] *Time of treatment, 4 hours.*

TABLE 9.—*Sulphur removal from large-size Pennsylvania gas-house coke (per cent).*

Sulphur as	Natural steam flow.[a]		Vacuum alternating with natural steam flow.		Vacuum alternating with steam under pressure.	
	Before treatment.	After treatment.[b]	Before treatment.	After treatment.	Before treatment.	After treatment.
Ferrous sulphide.........	0.43	0.24	0.24	0.17	0.41	0.22
Sulphates...............	0.00	0.00	0.00	0.00	0.00	0.00
Free sulphur............	0.38	0.36	0.18	0.05	0.25	0.09
Solid-solution sulphur....	0.59	0.59	0.72	0.72	0.80	0.80
Total sulphur..........	1.40	1.19	1.14	0.94	1.46	1.11

[a] *Natural steam flow, 10 cc. water as steam per gram of coke per hour.*
[b] *Time of treatment, 4 hours.*

The ferrous-sulphide sulphur was removed to a considerable extent, but this was not nearly as great as in the case of the fine-size tests. The greatest removal of this form was accomplished by the use of alternate pressure and vacuum, which eliminated approximately 50 per cent of the ferrous-sulphide sulphur from the Pennsylvania metallurgical and gas-house cokes. Illinois metallurgical coke gave up about 34 per cent under this method of treatment.

In none of the three cokes tested was there sufficient sulphate sulphur present to furnish results of any significance. From the fine-size tests it is evident that some of the sulphates are removed. How much of this form might be eliminated on the large-size coke cannot be stated. As the average metallurgical coke seldom carries any appreciable amount of sulphates, these figures would be of no material value had they been obtained.

A surprising feature of the results from the large coke will be noticed in the removal of free sulphur. From the fine-size tests we might expect that this form would be more obstinate than the ferrous sulphide, but the reverse was found to be the case. In none of the three cokes did the removal of this form drop under 50 per cent, and in the case of the Pennsylvania metallurgical coke it was entirely eliminated. This can best be explained as follows: A portion of the ferrous sulphide is enclosed in the coke walls, and therefore cannot be reached by the steam. In the case of the fine-size coke the walls were crushed, and practically all of the ferrous sulphide was made available to the action of the steam, whereas in the large-size coke this condition did not exist. On the other hand, the free adsorbed sulphur tends to spread evenly over the coke surfaces, so that if the sulphur be removed from one portion of the coke piece, more sulphur is transferred to that portion from the interior surfaces of the coke, which are not so readily reached by the steam flow. It would therefore be expected that the size of the coke pieces would not make so much difference in the case of free sulphur as in the case of ferrous sulphide.

It has already been definitely proved that the solid-solution sulphur is not affected by the steam until the coke itself is destroyed. Since the large-size tests were made with practically no coke-loss, it is safe to assume that there was no reduction in this form. In some cases the analyses showed an increase, which was due to the method of sampling, and is corrected in the tables as formerly explained.

TABLE 10.—*Comparative sulphur removal by various methods (per cent).*

Coke.	Natural steam flow.				Vacuum alternating with natural steam flow.				Vacuum alternating with steam under pressure.			
	Total sulphur.	Re-moved.	Re-movable sulphur.	Re-moved.	Total sulphur.	Re-moved.	Re-movable sulphur.	Re-moved.	Total sulphur.	Re-moved.	Re-movable sulphur.	Re-moved.
Illinois metallurgical coke	1.32	10.6	0.62	22.6	1.17	12.8	0.63	23.8	1.16	19.0	0.55	40.0
Pennsylvania metallurgical coke	0.95	12.6	0.29	41.4	1.09	13.8	0.33	45.4	1.09	19.2	0.31	67.7
Pennsylvania gas-house coke	1.40	15.0	0.81	25.9	1.14	17.5	0.42	47.6	1.46	24.0	0.66	53.0

Removable sulphur includes sulphur as ferrous sulphide, sulphates, and free sulphur.

The total sulphur removed varied from 15 to 25 per cent, depending upon the coke and the method of treatment. For example: Alternate vacuum and pressure caused the greatest removal in all cases; alternate vacuum and natural flow gave results only slightly below these; while natural flow was shown to be the poorest method of the three. In order to show this contrast more distinctly Table 10 was prepared.

The term "removable sulphur" refers to the sum of the ferrous sulphide, sulphates, and free sulphur. Since these are the forms attacked by the steam, any comparison of methods should be made on this basis rather than on the basis of total sulphur. It will be noticed that for all three cokes the use of vacuum alternating with pressure caused the greatest removal; however, the results obtained without the use of pressure are almost as good. It would seem, therefore, that the increase in sulphur removed can be charged principally to the use of vacuum rather than to the use of pressure. Pressure no doubt aids in forcing the steam into the interior of the piece, but if this space is completely evacuated the steam will penetrate without the aid of pressure.

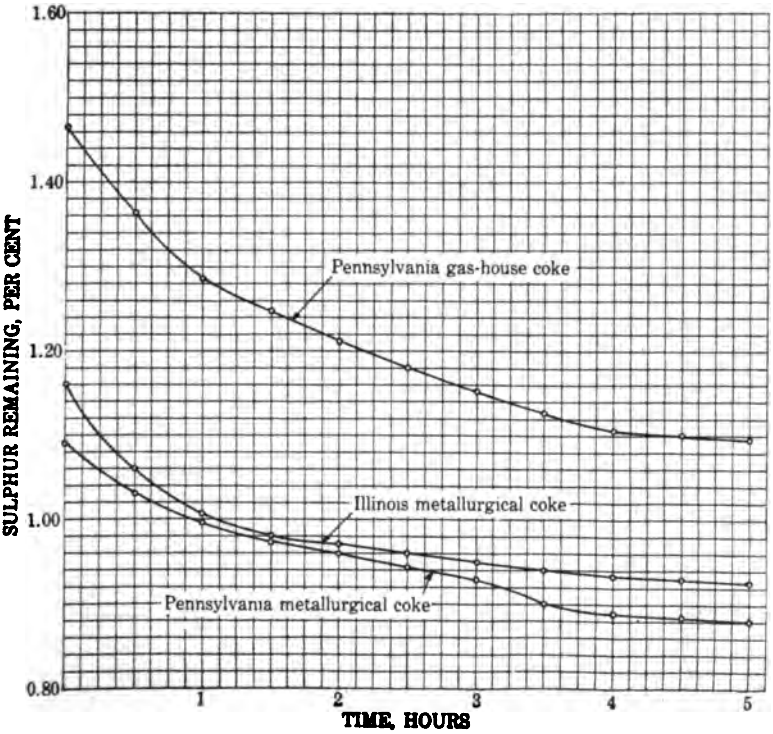

FIGURE 17.—*Rate of sulphur removal from large-size coke.*

In order to gain an idea of the time required, "rate of desulphurization" curves were prepared for each coke, and are shown in Figure 17. They show the removal throughout a 5-hour period, employing the use of alternate vacuum and pressure. It will be noticed that they have a gradually decreasing slope up to 4 hours, at which point they become almost horizontal. We may conclude therefore, that steaming beyond this time accomplishes little desulphurization. Similar curves were prepared employing the other two methods. These have much the same shape, except that they are not as steep at first, and fall above the ones here given for each respective coke.

As stated before, whenever natural steam flow was employed, a rate of 10 c.c. of water as steam per gram of coke per hour was used. This would correspond to 10 tons of water per ton of coke per hour. This of course was a large excess, and would be impractical on an industrial scale. An attempt was therefore made to determine the lower limit of the rate of flow. Theoretically, the quantity of steam should make no difference so long as there is enough passing through to react with the sulphur present and carry away the hydrogen sulphide. If this were true, the removal, other factors being held constant, for any two rates should be the same. This is providing, of course, that both rates furnish sufficient steam for the reaction, and also to act as a carrying agent. In order to check this point, a run was made using as little steam as possible, and another using a large excess. Illinois coke was used in both cases, and conditions were kept identical except for the flow of steam. In the first case, using a rate of 0.35 c.c of water per gram of coke per hour (700 lb. of water per ton of coke per hour) a removal of 33 per cent of "removable sulphur" was obtained. In the second case, with a flow of 10 c.c. of water per gram of coke per hour (20,000 lb. of water per ton of coke per hour) the corresponding removal was 31 per cent. This would seem to verify the foregoing conclusions.

Since the apparatus would handle only a few large pieces of coke, it was not thought practical to attempt an exact determination of the most efficient rate of flow. From the experience of the authors it is safe to state, however, that a rate of flow as low as 100 pounds of water per ton of coke per hour will accomplish as much desulphurization as will a higher rate. At times, during certain of the tests, the flow was cut to almost a negligible quantity, but no falling off in the percentage of sulphur removed, or any sudden breaks in the curves noticed.

ECONOMIC CONSIDERATIONS OF DESULPHURIZATION BY STEAM.

It is impossible without actual plant tests to estimate fairly the cost of desulphurization by steam. The following figures are merely an estimate, and should be considered at best as only a guess.

Steam.—As previously stated, 100 pounds of steam per ton of coke per hour will probably do the work as well as a larger quantity. A fair estimate as to the cost at which steam may be made is 20 cents per 1000 pounds. Since the process will not require over 4 hours, we may estimate the cost of the steam alone at approximately 8 cents per ton of coke treated. The steam may be superheated by passing it through the checker-work of the by-product coke-oven. The cost of superheating would thus be cut to a minimum, and should not run over 2 cents per ton of coke.

The treatment chamber.—Possibly the best method of steaming would be to treat the coke in a separate chamber. By this arrangement the coking time would not be affected, and the deleterious effects of the steam on the coke-oven refractories would be eliminated. This chamber should be designed with a capacity equal to that of one oven (10 tons). It should be constructed so as to afford efficient handling of the coke—possibly charging the coke at the top and drawing it at the bottom. The walls of the chamber should be of such nature that they will minimize radiation losses and retain the heat of the coke as long as possible. By preheating the steam to at least 600°, and charging the coke direct from the ovens, no external supply of heat would be required. Calculations on the specific heat of steam and of coke show that the coke under these conditions would not cool over 50° per hour. Thus the sensible heat of the coke would be sufficient to carry on the process.

It is of course impossible to state just what such a treating chamber would cost, but in the opinion of the authors it should not exceed $10,000, and its life should not be less than 5 years. Estimating that it would treat 60 tons of coke per day (24 hours), and assuming interest at 6 per cent, the depreciation and interest charges on such an investment would be about 11 cents per ton of coke treated.

Labor.—The only labor required for the process would be the transference of the coke from the oven to the chamber, and the operation of the chamber itself. By placing the treating chambers near the coke-ovens, the first item could be cut to not over 3 cents per ton. The operation of the chambers would be simple, and should not cost over 2 cents per ton.

Summary.—Bringing these three estimates together, the total cost of the process is shown to be 26 cents per ton of coke. In using these figures it should be remembered that the cost of the treating chamber is only a guess—it might exceed $10,000 and it might run considerably less. Also, since it is the surface sulphur that we seek to remove, the time might be cut from 4 to 2 hours, thereby effecting a reduction in the total cost of about 25 per cent. However, further study and an actual trial of steamed coke in the blast-furnace are needed before any exact figures can be given. It must be remembered that the primary object of this investigation was not to develop a steaming process for coke on an industrial scale, and under no considerations are these cost figures to be taken as representative of that.

COMPARATIVE STUDY BETWEEN STEAMED AND UNSTEAMED COKE, AS RELATED TO BLAST-FURNACE PRACTICE.

Recent studies[41] at the Pittsburgh Experiment Station of the Bureau of Mines have brought to light some interesting facts as to the probable behavior of steamed coke in the blast-furnace. The literature on the chemistry of blast-furnace reactions was thoroughly reviewed, and with this information in mind, the probable behavior of the cooke sulphur in the blast-furnace was deduced. Sufficient small-scale tests were conducted to furnish a check on most of the important deductions, and the conclusions derived therefrom are in accord with what is already known as regards the forms of sulphur in coke, and fit in well with the general opinion of the blast-furnace reactions. In general they are as follows:

REACTIONS IN THE REDUCTION ZONE.

1. In the reduction zone, the free sulphur and sulphates are reduced to ferrous sulphide. This fact is readily understood when we remember that the gases of this zone are highly reducing in character. As previously described under "analysis of sulphur forms," when the sulphates and free sulphur are subjected to a reducing atmosphere (hydrogen) at temperatures between 800 and 1000° they revert to their original form—namely, ferrous sulphide (FeS). Thus the reduction made in analyzing is a small-scale duplicate of the reduction zone of the blast-furnace.

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[41] Powell, A. R., Forms of sulphur in coke and their relations to blast-furnace reactions: To be published in Trans. Amer. Inst. Min. & Met. Eng., vol. 69, 1923, 13 pp.

Thompson, J. H., Forms of sulphur in steamed coke, and their action in the blast-furnace: Reports of Investigations, Bureau of Mines, Serial No. 2518, Aug., 1923, 7 pp.

REACTIONS IN THE SPONGY-IRON ZONE.

2. In the zone of spongy iron, a considerable amount of sulphur is taken up by the iron from the coke. The ferrous-sulphide constituent of the coke is the form that gives up sulphur at this point. This zone is therefore of considerable interest as regards the contamination of the iron by sulphur, but some doubt seems to exist as to just what really does happen therein, and small-scale tests were made to check the above conclusion. These are described herewith:

(a). The iron used consisted of short lengths of iron bailing wire. In making a test, a definite weight of this iron was buried in a small quantity of granular coke in a crucible, which was covered so that there would be no free access of air, and was then heated to a bright red heat in a muffle furnace. Under these conditions the atmosphere would quickly become reducing, due to the formation of carbon monoxide and smaller quantities of carbon dioxide. After cooling, the iron was removed and analyzed for sulphur.

The first coke was high in sulphur, containing over 3 per cent of total sulphur. One batch of this coke had been previously oxidized at about 500°, and it was found that this treatment completely oxidizes the ferrous sulphide, so that the coke so treated contains only solid-solution sulphur and free adsorbed sulphur, plus a small quantity of sulphate. Another batch was reduced by hydrogen so that it would contain only solid-solution sulphur and ferrous sulphide. In this way the relative effect of the two forms—namely, free sulphur and ferrous sulphide—could be studied. It was assumed (and later tests showed this assumption to be correct) that the solid-solution form of sulphur would be inert, and would have no action on the iron. The results of this test were as follows:

	Oxidized coke, sulphur, %.	Reduced coke, sulphur, %.
Sulphur content of original iron....................	0.064	0.064
Sulphur content of iron after treatment..............	0.219	0.215

These results bring out two facts: In the first place, a rather large amount of sulphur is taken up by the iron when in contact with the coke; and secondly, the relative amounts of ferrous sulphide and free sulphur in the coke do not affect the absorption of sulphur. This latter fact is to be explained on the basis of the reducing atmosphere in the crucible, and the consequent reduction of any free sulphur to ferrous sulphide. This confirms the statement made earlier, that any free sulphur in the coke is quickly changed to ferrous sulphide in the reduction zone of the furnace, and that the sulphur which the iron takes from the coke comes from the ferrous sulphide.

(b). Another set of experiments was conducted, in which an effort was made to maintain a slightly oxidizing influence in the red-hot crucible containing the coke. This was accomplished by leaving off the lid of the crucible so that the coke would have free access to the air. In this case the Illinois coke previously mentioned was used. This coke, as may be seen by referring to the analysis, contained about 1.30 per cent of sulphur, and was therefore more like an ordinary metallurgical coke. To bring out the relative effect of the oxidizing atmosphere, a test in a covered crucible was run parallel with this, and the following results were obtained:

	Crucible covered reducing, %.	Crucible uncovered oxidizing, %.
Sulphur content of original iron	0.064	0.064
Sulphur content of iron after treatment with coke	0.241	0.339

These results show that an oxidizing atmosphere tends to throw more sulphur into the iron, which was to be expected when it is considered that free sulphur, with its comparatively high vapor pressure, would be formed under such conditions. Another fact brought out by this experiment was the comparative amount of sulphur introduced into the iron by this coke, and the higher sulphur coke used in the first experiment. About the same quantity of sulphur was given up to the iron by the lower sulphur coke as by the higher sulphur coke, even under reducing conditions. However, an equal absorption might be expected when it is considered that the pressure of free sulphur vapor over the coke is independent of the amount of sulphur contained in the coke, since ferrous sulphide will exhibit the same dissociation pressure for any given temperature, regardless of the quantity of ferrous sulphide present. The limiting factor which determines how much sulphur will be taken up by the iron in the sponge-iron zone of the furnace is therefore not necessarily the amount of sulphur in the coke, but is probably the speed with which the ferrous sulphide formed at the surface of the iron diffuses into the interior of the iron. In this connection it must be remembered that the spongy iron of the blast-furnace offers a large surface for the absorption of sulphur.

(c). It was expected that the solid-solution form of sulphur would be practically inert under these conditions, so in order to determine this by actual experiment, the Illinois coke was reduced by hydrogen, and then treated with boiling hydrochloric acid. This treatment removed from the coke all forms except the solid-solution sulphur. The following results were obtained in this case:

	Sulphur, %.
Sulphur content of original iron	0.064
Sulphur content of iron after exposure to coke	0.083

Comparison of this result with those obtained from the coke in which the ferrous sulphide was present shows a great difference in the amount of sulphur absorbed. In fact, it is doubtful whether the small quantity of sulphur taken up from the above coke came from the solid-solution form, and it is more probable that this came from the small quantity of ferrous sulphide which was left in the coke after the acid treatment.

It must also be remembered that in addition to the spongy iron and the coke, lime is present in this zone of the blast-furnace. Tests were made in which lime was mixed with the coke, in which the iron was buried; under these conditions the lime would be in more intimate contact with the coke than the iron. The results from several tests showed that practically no sulphur was taken up by the iron, all of the sulphur given off by the coke being absorbed by the lime. However, the relative intimacy of contact between the lime and the coke was greater in these cases than would be the case in the blast furnace, so it must not be assumed that the lime in the spongy-iron zone would entirely protect the iron from contamination by sulphur. The results obtained were as follows:

	Original coke, %.	Coke, with lime, %.	Coke with magnesia, %.	Coke with soda, %.
Sulphur content of original iron	0.064	0.064	0.064	0.064
Sulphur content of iron after exposure to coke	0.462	0.076	0.098	0.098

The great difference between the amount of sulphur absorbed by the iron from the untreated coke and the small amount from the limed coke is apparent at once. It will be noted that magnesia and soda are also effective in preventing the sulphur from going into the iron. In every case the corresponding metallic sulphide has been formed, all of which have dissociation pressures far below that of ferrous sulphide.

REACTIONS IN THE ZONE OF PRELIMINARY SLAG FORMATION.

3. In the zone of preliminary slag formation, the absorption of sulphur by the iron is largely prevented. In this region the lime begins to unite with the silicious impurities of the iron, and the result is a viscous limey slag, which will have a tendency to coat the iron and also the coke. When this occurs, the transfer of sulphur from the coke to the iron will be practically stopped.

REACTIONS IN THE COMBUSTION ZONE.

4. In the combustion zone, the sulphur released from the coke is probably absorbed by the slag. In this region of the furnace the slag also removes the excess sulphur from the iron, which entered the iron in the spongy-iron zone. This reasoning is based on the intimacy of contact, since the drops of liquid iron are to some extent surrounded by the slag. Of more importance than this, however, is the fact (borne out by actual observation[42]), that the coke, just before combustion, becomes impregnated with the slag. This is an important point, because the major portion of the coke sulphur is released at this stage of the process, and the conditions would seem to be ideal for its complete absorption by the slag.

An interesting case which would seem to prove the correctness of almost all of the conclusions made here, and taken from an actual blast-furnace run, has recently been brought to light. R. H. Sweetser, of the American Rolling Mill Co., at Columbus, Ohio, reports the following interesting figures: Trouble with one of the blast-furnaces made it necessary to shut down. The furnace was quenched, and samples were taken of the products therein. A sample of the spongy iron taken just above the bosh gave 0.136 per cent of sulphur. The sulphur analysis of the pig product by this furnace just previous to the shut-down was 0.022 per cent. Coke taken from the combustion zone was found to be impregnated with the slag to a marked extent. In general, therefore, the conclusions formerly drawn would seem to be in agreement with actual conditions in the blast-furnace.

It will be noticed that the chief contaminating substances in coke were the free sulphur and the ferrous sulphide. Since these two forms are those which steam most readily attacks, it would seem only natural that steaming the coke would considerably lessen the contaminating influence of sulphur on the iron. No doubt the removal of these two forms by steam is far greater at the surface of the piece than at the interior, and since this contamination is a contact phenomena, this surface removal would be another favorable feature. We should therefore expect steamed coke to give up far less sulphur to the iron than the comparative total sulphur figures would indicate.

---

[42] Imhoff, W. G., Sulphur as a component of surface slag: *Blast Furnace & Steel Plant*, vol. 51, 1917, pp. 358-362; also *Chem. & Met. Eng.*, vol. 17, 1917, pp. 189-190.

TESTS TO SHOW HOW MUCH SULPHUR IS GIVEN UP BY COKE TO IRON IN THE FURNACE.

With a view to checking this point, and also to more nearly duplicate blast-furnace conditions than previously described, several tests were made on both steamed and unsteamed coke. The coke used contained over 3 per cent total sulphur, this being selected because a comparison only was sought, and the high-sulphur content should result in quantities which could be more easily measured.

Actual spongy iron was obtained from the Northwest Station of the Bureau of Mines at Seattle, Washington. This material was made by reducing the iron ore in a kiln, by means of an external supply of heat. It contained 0.38 per cent of sulphur, and with the exception of about 5 per cent of impurities—chiefly carbon—was the same as the sponge iron of the blast-furnace. The high sulphur content made posible a study of the sulphur transfer from the iron into the lime, as well as from the coke into the iron.

The same coke was used throughout, the only difference being that in one case it was steamed and in the other unsteamed. This steaming was conducted on pieces of plus ½ inch and minus 1-inch sizes. Neither vacuum or pressure was used, and the removal was therefore more or less confined to the surface of the piece. The tests were conducted as follows:

Test No. 1.—Unsteamed coke (150 grams) was mixed with 350 grams of the sponge iron in a cast-iron tube closed at one end, the large excess of iron being necessary to get complete contact with all of the coke pieces. The tube was then placed in the retort already described. Air was prevented from circulating through the retort, the only opening being the ¼-inch outlet at the top. Reducing conditions were thus obtained. The current was turned on, and the retort brought to 1000° in about 3 hours. This temperature was then held constant for a period of 4 hours, after which is was allowed to cool. When cool, the tube was removed, the coke was separated from the iron by screening, and both products were analyzed.

Test No. 2.—This test was essentially the same as No. 1, except that in this case steamed coke was used rather than unsteamed.

Tests No. 3 and 4.—These were respectively similar to No. 1 and 2, except that in these cases 100 grams of powdered lime (CaO) was mixed with the sponge iron before charging. The lime was separated from the iron by means of a magnet. In every case sulphur analyses were made on all products before and after treatment. The results obtained are summarized in Table 11, following:

TABLE 11.—*Comparative study between steamed and unsteamed coke.*

The coke.

Sulphur as.	Unsteamed coke, %.	Steamed coke, %.	Sulphur removed, %.
Ferrous sulphide	0.41	0.30	26.8
Sulphates	0.00	0.00	....
Free sulphur	0.89	0.40	53.9
Solid solution	2.03	2.03	00.0
Total sulphur	3.33	2.73	18.0
Removable sulphur*	1.30	0.70	46.1

**Removable sulphur includes sulphur as ferrous sulphide, sulphates, and free sulphur.*

The iron and lime.

	Sulphur before treatment, %.	After treatment, unsteamed coke with sponge iron, %.	After treatment, steamed coke with sponge iron, %.	After treatment, unsteamed coke with sponge iron and lime, %.	After treatment, steamed coke with sponge iron and lime, %.
Spongy iron	0.38	0.69	0.48	0.36	0.29
Lime	0.00	....	....	1.12	1.34

A distinct contrast will be noticed in all cases between the action of the steamed and unsteamed coke. Without lime present, the sulphur of the iron increased from 0.38 to 0.69 per cent, in the case of unsteamed coke. Blast-furnace practice today bases its expected sulphur trouble on the relative amount of total sulphur in the coke. Using this criterion we should expect the steamed coke to show an improvement of 18 per cent, since this is the percentage of total sulphur removed by steam. In other words, the sulphur content of the iron after treatment with steamed coke, using this basis, should be approximately 0.63 per cent; but in reality it is found to be only 0.48 per cent.' Where we might expect an improvement of 18 per cent we actually obtained one of 67 per cent.

Runs No. 3 and 4, using lime, seem to show these same general phenomena. It will be noticed that even in the case of unsteamed coke the iron was slightly desulphurized, this being due to the intimate contact between the lime and the sponge iron. Such conditions do not prevail in the blast-furnace; and as shown before, the iron does become contaminated with sulphur, even though there be lime present. In test No. 4, using steamed coke and lime, desulphurization of the iron is much greater than in the case of unsteamed coke. Since the sulphur has been removed from the surface of the coke chunk by steaming the lime is not contaminated by this sulphur to the extent that it was with unsteamed coke, so it can therefore more efficiently desulphurize the spongy iron. Steaming the coke would thus be twofold in its benefits: first, the spongy iron would not be nearly so heavily laden with sulphur; and secondly, the lime would in like manner come through with less sulphur, and would therefore be in much better condition to desulphurize the iron at the combustion zone. These figures would seem to suggest two possible methods for correcting the sulphur trouble in the blast-furnace; first, this surface sulphur could be removed by some such process as steaming; or secondly, it could be prevented from entering the spongy iron at this zone by dipping the coke in some material which would absorb the sulphur more readily than would the iron. Possibly lime could be used in this case; but whatever the nature of the substance it should be such that it will not interfere with the proper conbustion of the coke at the combustion zone. Further studies along this line would no doubt lead to some interesting discoveries as to the behavior of the sulphur in the blast-furnace.

SUMMARY OF GENERAL INVESTIGATION.

The work on the desulphurization of coke may be summarized briefly as follows:

1. Steam does desulphurize coke, but a complete removal is impossible.
2. Vacuum, alternating with steam under pressure, gave the maximum removal. This method removed between 20 and 25 per cent of the total sulphur.
3. Vacuum, alternating with natural steam flow, removed between 15 and 20 per cent of the total sulphur. Of the two factors —vacuum and pressure—the former is much greater aid to desulphurization than the latter.

4. Natural steam flow resulted in a removal of between 10 and 15 per cent of the total sulphur.

5. The optimum temperature for the process is about 750° C.

6. The time required to obtain the aforementioned removals is between 2 and 4 hours, depending upon the method used.

7. The quantity of steam has practically no effect upon the rate of removal of the total amount removed. Fifty pounds of water as steam per ton of coke per hour will probably result in just as efficient a removal as will a much larger volume.

8. It seems highly probable that the relative improvement in the coke for metallurgical purposes by steaming should not be measured in terms of the total sulphur removed. The contaminating influence of the sulphur upon the iron would seem to be more a function of the surface sulphur than of the total sulphur in the coke. The improvement, therefore, can be best determined in terms of this particular part of the sulphur—namely, the ferrous sulphide and free sulphur on the surface of the piece of coke.

CONCLUSIONS.

1. In general, it would seem that, so long as the supply of low-sulphur coals is available, the steaming of coke could not be termed an industrially feasible process. However, when it becomes necessary to resort to the use of higher sulphur coals for the manufacture of coke, the improvement of the coke through steaming may be of sufficient value to warrant the expense of the process. It is safe to state that, of the many processes thus far tried, steaming results in the greatest removal, and offers the best possibilities for adaption to the coke industry.

2. The recent work of the authors on the behavior of sulphur in the blast-furnace would seem to show that steamed coke is a decidedly better metallurgical fuel than its total sulphur content would indicate; but further study as to the behavior of the forms of sulphur in the blast-furnace is needed before any definite statement as to the actual benefits of steaming can be made.

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Bulletin 8

COAL-MINING INVESTIGATIONS

UNDER AUSPICES OF

CARNEGIE INSTITUTE OF TECHNOLOGY,
U. S. BUREAU OF MINES, AND
ADVISORY BOARD OF COAL-MINE OPERATORS AND ENGINEERS.

THE LOW-TEMPERATURE CARBONIZATION OF PENNSYLVANIA COALS—THE PITTSBURGH AND UPPER KITTANNING BEDS.

By

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CARNEGIE INSTITUTE OF TECHNOLOGY,
PITTSBURGH, PENNSYLVANIA,
1923.

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PREFACE.

Pittsburgh is the greatest industrial center in America, and the heart of the greatest bituminous coal-mining district in the world. It is eminently desirable, therefore, that this city should have an institution which devotes a part of its great facilities to the scientific study of that branch of the industry which is largely responsible for Pittsburgh's development and that of western Pennsylvania.

On May 27, 1919, a number of leading representatives of the coal-mining industry of western Pennsylvania met in conference with the President of Carnegie Institute of Technology with a view of bringing about closer relations between the Institute and the mining interests. It was felt that the advice and co-operation of men in the field were necessary for the training of young men for mining work, and at the conclusion of the meeting the following resolution was adopted:

> That this gathering give its approval and moral and material support to the form of education proposed for the Carnegie Institute of Technology by which students may receive a combined technical, practical, and business training, necessary to fit them for service in the coal mining and allied industries. Further, that the President of the Carnegie Institute of Technology appoint a board of no less than ten men representing the coal mining and allied industries, the United States Bureau of Mines, the State Department of Mines, and the Carnegie Institute of Technology, who will advise and assist in carrying out this program of education and training, particularly in its practical phases to the mining industry and in its co-operation with the United States Bureau of Mines.

Following further the intention of this resolution, the President of the Institute entered into a co-operative agreement on June 1, 1919, with the Director of the U. S. Bureau of Mines whereby full advantage could be taken of the Bureau's laboratories, equipment, and library, as well as of the advice and instruction of its technical staff.

To carry out this new program there was organized during the summer months the Co-operative Mining Courses in the Department of Mining and Metallurgical Engineering, College of Engineering, of the Institute. The course in mining engineering covers four years, and leads to the degree of Bachelor of Science. The two-year course in coal mining is planned to prepare men

with a certain amount of practical experience for executive positions. The four-weeks intensive summer course in coal mining is designed for miners who aspire to be firebosses and mine foremen.

In a large measure, the new mining, ore-dressing, and coal-washing laboratories at the Institute have been equipped gratuitously by various manufacturers of mining machinery and appliances. Co-operative research through teaching and research fellowships is devoted to various problems in coal mining and the utilization of fuels. The Institute selects the fellows, the Bureau of Mines provides the laboratory facilities, and the Advisory Board determines what problems be undertaken, and publishes the reports.

The primary object of this co-operation of the Carnegie Institute of Technology, the U. S. Bureau of Mines, and the Advisory Board of Coal Mine Operators and Engineers is the proper education and training of young men for the mining industry. The ultimate objective is to bring about better conditions and greater efficiency in mining operations. The decrease in reserves of coal and increasing cost of production make it urgently necessary for mine operators and engineers to take advantage of everything which modern science, machinery, and methods can contribute.

EDWARD STEIDLE,
Supervisor, Co-operative Mining Courses,
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FOREWORD.

The investigation described in this paper was conducted by the Co-operative Mining Courses of the Department of Mining of the Carnegie Institute of Technology and the Pittsburgh Experiment Station of the U. S. Bureau of Mines, in co-operation with the coal-mining industry of western Pennsylvania. Under co-operative agreement, four research fellowships paying $750 per school year of 10 months are supported by the Carnegie Institute. These fellowships are open to properly qualified graduates of universities and technical schools. The research work is carried on in the laboratories of the Bureau of Mines under the direction of a member of the Bureau research staff, and results are published under the joint authorship of the two investigators.

Fellowship holders are required to register at the Institute as graduate students and become candidates for the degree of Master of Science, unless an equivalent degree has been previously earned. The purpose of these fellowships is the solution of problems in mining and utilization of coal.

This bulletin is the second publication on the low-temperature carbonization and by-product yield of western Pennsylvania coals. Bulletin 1 gave the yield and quality of the gas, oil, and other by-products of the constituents of the Freeport coal bed. This bulletin (No. 8) includes similar tests of the Pittsburgh and Upper Kittanning beds. Special attention has been given to the composition of the low-temperature tars and their possible industrial utilization. The Kittanning coal was not suitable for low-temperature carbonization, but the Pittsburgh coal, including the "rooster" coal, the lower roof, and the upper roof yielded low-temperature coke of good domestic quality and a satisfactory quantity of low-temperature tar. A total yield of 7.1 gallons of crude motor fuel oil per ton was obtained.

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THE LOW-TEMPERATURE CARBONIZATION OF PENNSYLVANIA COALS—THE PITTSBURGH AND UPPER KITTANNING BEDS.

By J. D. DAVIS *and* V. FRANK PARRY.

INTRODUCTION.

Research on the low-temperature carbonization of coal has been in progress for a number of years, the main object being to produce a coke more suitable for domestic use than the high-temperature product of the gas-works and coke-oven, and at the same time to effect a higher recovery of constituents in the tar oils. Much valuable data have been accumulated, but this has not as yet led to any industrial development worth mentioning in the United States. Since the World War, investigators have been particularly active in England, where one of the main incentives is the production of fuel oil for which that country would like to develop a domestic source. Presumably there is also a good demand for low-temperature coke for open fires in English homes. In Germany, during the war, research on low-temperature tar oils was carried on intensively on account of the demand for lubricants, substitutes for mineral oils, which can be made from refined tars. Considerable quantities of lubricants were made from such tars during that period, but it is doubtful whether these are competing now with imported petroleum oils. Obviously there must exist a definite demand for low-temperature products before any extensive development of the method can be expected. The abundant supply of petroleum in the United States, and like supply of coal suitable for high-temperature coking, would seem to preclude competition of low-temperature products in either field in the near future. There is, however, a strong possibility of better utilization of waste coals and coals of inferior rank by low-temperature methods, and this phase of the subject should be a fruitful field for research. Further, the utilization of low-temperature tar oils for special purposes, as, for example, for the preservation of timber, is a reasonable expectation; as is also the improvement of high-temperature coke by preliminary low-temperature treatment. These points have yet to be proved industrially practicable.

Pennsylvania ranks first among the States in the production of coal and coke, and is therefore vitally interested in research pertaining to the improvement of their utilization. By co-operative agreement of certain coal-mining companies, the Carnegie Institute of Technology and the Bureau of Mines, investigations are being made into low-temperature carbonization of typical Pennsylvania coals, particularly as regards the utilization of low-grade coals—that is, parts of the beds that are not mined at present because they can not be marketed in competition with the better quality coal. These investigations have been in progress since July, 1921. The first year's work comprised a study of coals from the complete Thick Freeport bed[1]; while this year the work has been extended to include a study of coals from the Pittsburgh and Upper Kittanning beds.

ACKNOWLEDGMENTS.

The writers wish to express their appreciation for the helpful suggestions of A. C. Fieldner; to O. P. Hood, chief mechanical engineer of the Bureau; and for the valuable assistance rendered by J. J. Jakosky, assistant engineer at the Pittsburgh Station of the Bureau, in the evaluation of tar oils. They also take this opportunity to acknowledge the excellent co-operation and help given by the officials of the mines from which the coal samples were obtained. The manuscript was also carefully read by H. N. Eavenson, to whom thanks are due.

For procuring samples of coals we are indebted to Messrs. G. S. Baton and J. R. Elliott, consulting engineers for the Greensburg-Connellsville Coal & Coke Co., also to P. O. McKinney, superintendent for the Ford Collieries Co., whose mines are mentioned later.

PURPOSE OF INVESTIGATION.

The investigation made during 1921 included a study of coal from the Thick Freeport bed, with particular reference to the yield of by-products and the quality of the oils from the bony partings of the seam; while the investigation made during 1922 and 1923 extended the work to include a comparison of by-product yields from Pittsburgh and Kittanning coals, with those from the Thick Freeport bed.

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[1] The yield and quality of the gas, oil, and other by-products of the constituents of the Freeport coal bed, Pennsylvania, by J. D. Davis and H. G. Berger: Bull. 1. Carnegie Institute of Technology, 1922, 43 pp.

The purpose of the present investigation is as follows:

1. To study the low-temperature carbonization products from all parts of the Pittsburgh bed, which includes the regular coal that is mined, the rooster coal, and two partings of the roof coal which are of rather poor quality.

2. A comparison of the Pittsburgh, Freeport, and Upper Kittanning coals under similar methods of carbonizing—namely, at 550° C.; and to study the characteristics of the by-products from the three coals, and to improve methods for the rational analysis of the tars.

3. A study of the tars obtained, with particular reference to the recovery of maximum amount of light oils suitable for motor fuel, (a) by straight distillation of the tar, (b) by cracking of the heavy neutral oil, and (c), by reduction of the tar acids.

4. To study the effects of superheated steam on the yield and quality of the by-products.

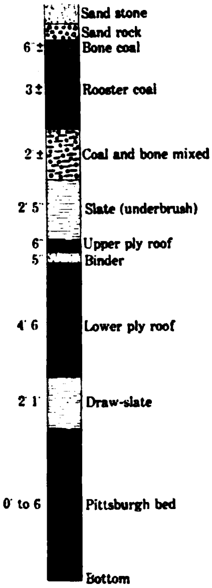

FIGURE 1.—*Cross section of Pittsburgh bed, Burgettstown, Pa.*

SOURCE OF COALS INVESTIGATED.

Pittsburgh coal.—Samples from the Pittsburgh bed were obtained at the Francis mine, Burgettstown, Pa., operated by the

Greensburg-Connellsville Coal & Coke Co. Four sections of the bed were sampled. The lower bench of the bed, which is the section chiefly mined, is bituminous coking coal, high in volatile matter and low in ash. It is about 60 inches thick. The other sections sampled were the rooster, the upper roof, and the lower roof. These coals are fairly similar to that mined, but are higher in ash and sulphur. Table 1 gives an analysis of these coals, while Figure 1 shows a cross section of the Pittsburgh seam as it lies at Burgettstown.

Freeport coal.—Samples of the upper and lower benches of the Thick Freeport bed were obtained from Francis mine No. 2 of the Ford Collieries Co., at Curtisville. These samples represent the part of the bed that is mined. The upper bench is 33 inches and the lower bench about 35 inches thick and are separated by a layer of bone coal. Table 1 also gives an analysis of this coal.

Upper Kittanning coal.—A sample of Upper Kittanning coal was obtained from the Hillman Coal & Coke Co., at Jerome, Pa. This is a semi-bituminous coal, low in volatile matter and high in fixed carbon.

IMPORTANT FACTORS IN THE LOW-TEMPERATURE CARBONIZATION OF COAL.

Coal is so sensitive to conditions of retorting for low-temperature products that innumerable combinations of by-products can be obtained. During recent years, especial attention has been paid to low-temperature methods of destructive distillation, and many companies are investigating their possibilities on a semi-industrial scale. Some of these investigators are working for smokeless fuel as the main product, such as the "carbocoal" process of the International Coal Products Co. Others pay particular attention to the yield and quality of the tar, this being particularly true in Germany where petroleum is not nearly so plentiful as it is in America. Again, some investigators work for the best combination of the yield of coke and tar, with equal attention paid to both, this no doubt being the most desirable solution of the low-temperature problem.

Fisher[2] warns against a general rush into the manufacture of low-temperature tar before the technical questions connected with

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[2] Fischer, Franz, Over-valuation and under-valuation of low-temperature tar: *Brennstoff Chem.*, vol. 1, 1920, p. 69.

TABLE 1.—*Analyses of coals studied.*

Bed and Place.	Proximate Analysis.				Ultimate Analysis.					Calorific value, B. t. u.
	Moisture.	Volatile matter.	Fixed carbon.	Ash.	Hydrogen.	Carbon.	Nitrogen.	Oxygen.	Sulphur.	
Pittsburgh bed, Burgettstown, Pa.	(a) 4.6	35.4	49.5	10.5	5.4	69.1	1.3	11.1	2.6	12440
	(b) 2.3	36.3	50.6	10.8	5.2	70.8	1.3	9.2	2.7	12750
	(c) ...	37.1	51.9	11.0	5.1	72.5	1.3	7.4	2.7	13040
	(d) ...	41.7	58.3	....	5.7	81.4	1.5	8.3	3.1	14660
Pittsburgh rooster coal, Burgettstown, Pa.	(a) 1.4	32.7	48.3	17.6	4.6	64.9	1.4	9.0	2.5	11920
	(b) ...	....	....	....	...	....	...	...	...	.....
	(c) ...	33.2	48.9	17.9	4.5	65.8	1.4	7.8	2.6	12090
	(d) ...	40.4	59.6	....	5.5	80.1	1.7	9.6	3.1	14730
Freeport coal, upper bench, Curtisville, Pa.	(a) 1.5	39.2	54.7	4.6	5.5	78.9	1.7	7.5	1.8	14240
	(b) 1.1	39.4	54.9	4.6	5.5	79.2	1.7	7.2	1.8	14290
	(c) ...	39.8	55.5	4.7	5.4	80.1	1.7	6.3	1.6	14450
	(d) ...	41.7	58.3	....	5.7	84.0	1.8	6.6	1.9	15150
Pittsburgh roof coal, upper ply, Burgettstown, Pa.	(a) 2.6	31.1	43.7	22.6	...	....	...	...	...	.....
	(b) 1.0	31.6	44.4	23.0	...	....	...	...	...	.....
	(c) ...	31.9	44.9	23.2	...	....	...	...	...	.....
	(d) ...	41.5	58.5	....	...	....	...	...	...	.....
Pittsburgh roof coal, lower ply, Burgettstown, Pa.	(a) 3.2	35.9	49.1	11.8	5.2	69.5	1.4	10.3	1.8	12480
	(b) 1.3	36.7	50.0	12.0	5.1	70.9	1.5	8.7	1.8	12730
	(c) ...	37.1	50.7	12.2	5.0	71.8	1.5	7.7	1.8	12900
	(d) ...	42.3	57.7	....	5.7	81.8	1.7	8.7	2.1	14690
Lower Freeport coal, Francis mine, Curtisville, Pa.	(a) 2.5	36.5	57.2	3.8	5.5	79.2	1.6	8.6	1.3	14170
	(b) 1.5	36.9	57.7	3.9	5.4	80.0	1.6	7.8	1.3	14330
	(c) ...	37.4	58.7	3.9	6.3	81.2	1.6	6.7	1.3	14540
	(d) ...	30.9	61.1	....	5.5	84.5	1.7	6.9	1.4	15130
Upper Kittanning coal, Jerome, Pa.	(a) 0.1	18.3	76.1	5.5	...	....	...	...	...	...
	(b) ...	....	....	....	...	....	...	...	...	...
	(c) ...	18.3	76.2	5.5	...	....	...	...	...	...
	(d) ...	19.4	80.6	....	...	....	...	...	...	...

(a) *As received basis.*

(b) *Air-dry basis.*

(c) *Moisture-free basis.*

(d) *Ash and moisture-free basis.*

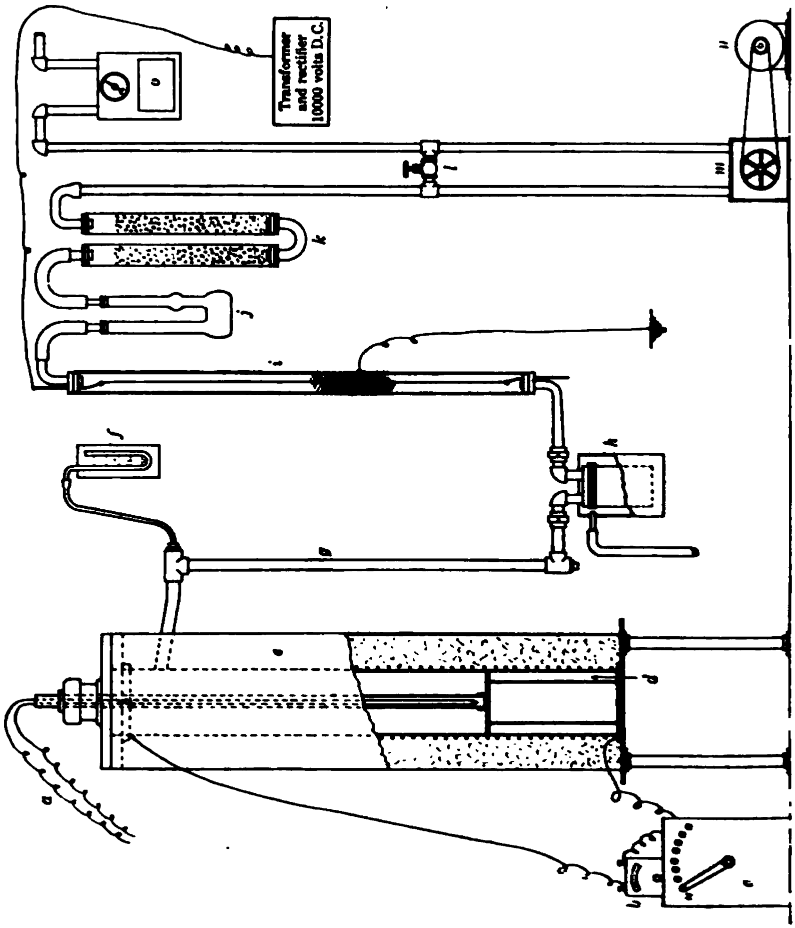

FIGURE 2. Diagram of apparatus for the low-temperature carbonization of coal.

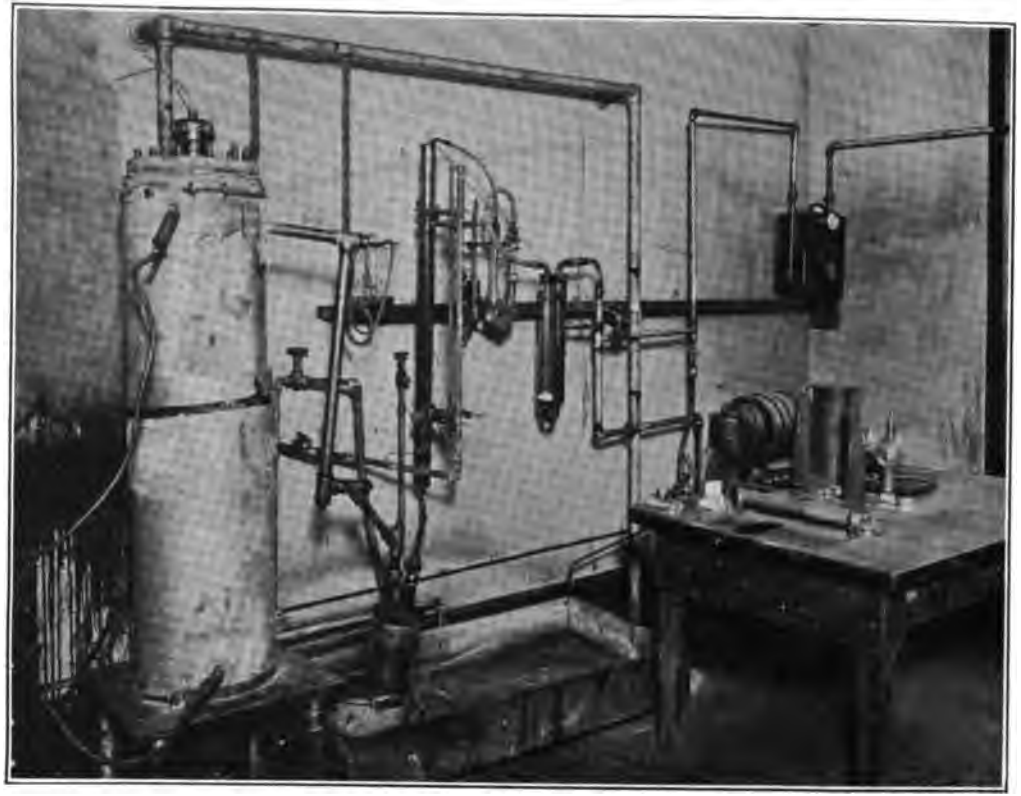

FIGURE 3.—*View of apparatus as set up.*

its utilization have been further investigated. To quote Fischer:

> In only a few cases can it [the tar] be utilized, and if the market is flooded with it as a raw material before chemical and petroleum industries are ready for its use on a large scale, the industry will receive a severe set-back.

Many of the investigators working on a semi-industrial scale use retorts handling a moving mass of coal, a continuous process being desirable in order to obtain high carbonization capacity. Most of the small-scale investigators have worked with a retort that held the coal stationary owing to mechanical difficulties attending the moving arrangement. As a result, the yield and quality of the by-products from the two systems are not exactly comparable, although the temperature of distillation is the same. In the continuous process, the coal is distilled at a much faster rate, and the vapors are swept from the retort before much secondary reaction has taken place. This is due to the uniform distribution of the heat throughout the coal mass. When coal is distilled in a stationary retort, the conditions are changed materially; the low heat conductivity of the coal causes slower evolution of the tar vapors and a longer contact with the retort walls, a condition which produces secondary reactions thus altering the products. Also, there is uneven heat distribution.

EXPERIMENTAL WORK.

DISTILLATION APPARATUS.

The apparatus used is shown in Figures 2 and 3. This equipment is the same as that used by Davis and Berger[3] in previous work on the Freeport bed. The coal was distilled in the electrically heated retort *e*, which is 6 inches in diameter. A shelf was placed in the retort and held up by a sleeve *d* to protect the coal from the cold end. At *c* is a regulating transformer for temperature control, and *b* is an ammeter. Two chromel-alumel thermocouples were placed in the coal, one in the center of the charge and the other at the wall adjacent. A Leeds and Northrup potentiometer was used for temperature measurements.

A charge of coal weighing 15 pounds, ground to about ¼ mesh, was placed in the retort. The bottom of the charge was 14 inches from the cold end of the retort, while the top level was 15 inches below the discharge. The mass of coal was heated as rapidly as possible until the thermocouple at the wall registered 500° C. Then the heating was carefully regulated so that the wall temperature reached and remained at 550°. This temperature was chosen somewhat arbitrarily, but with a view to obtaining a high yield of light oils. The previous work[4] showed a lower yield of light oils than was expected, and it was believed that the distillation temperature of 600° was too high. That 550° was the better temperature in this regard will be shown in what follows. Two hours were required to bring the wall temperature up to 550°, while the center of the coal mass required five hours to come to equilibrium. The lag in the temperature varied from 2 to 3 hours between the center and the wall. Figure 4 gives the variation of retort temperatures with time, and shows the distribution of distillation products throughout the carbonization process.

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[3] Work cited.

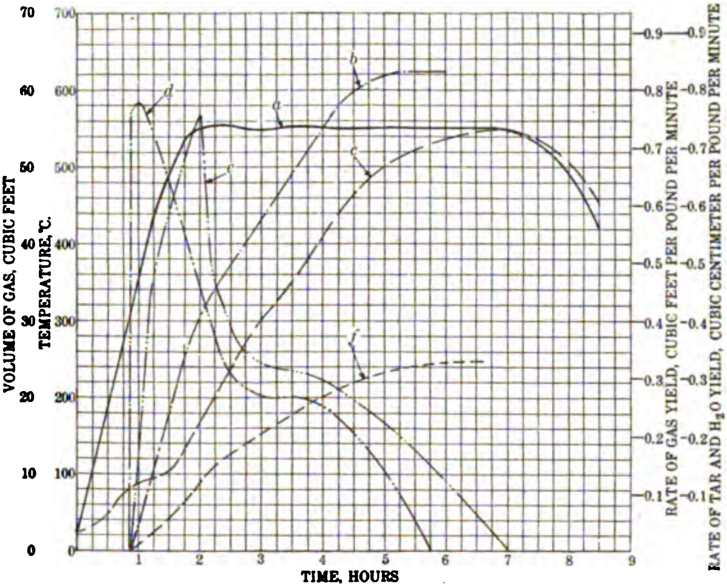

FIGURE 4.—*Temperature distribution and yield of tar and gas in low-temperature carbonization at 550° C. in vertical retort.*

Reference to letters on curves: *a*—temperature of outer wall; *b*—yield of tar plus water; *c*—center temperature; *d*—rate of yield of tar plus water; *e*—rate of yield of gas; *f*—gas yield.

All of the coals were tested under the same conditions, as shown by the figure. These conditions were necessarily the same for comparative work because of the great temperature sensitivity of coal at these low temperatures; a slight variation of the temperature has a distinct bearing on the yield and quality of the by-products, causing disproportionate changes. Much has been written of the characteristics of low-temperature tar oils, but the results are more or less confusing on account of indefinite statements as to the exact conditions of carbonizing. By referring to Figure 4 we can follow the process of carbonization.

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[4] Work cited.

Tar and gas make their appearance when the wall temperature reaches 350°, and their evolution continues for 4 hours, or until the temperatures at the center and at the wall are equalized. The break in the middle temperature curve shows the distillation of the water of composition, and from there on the temperature rises uniformly. The complete removal of the water of constitution is shown by the break in the yield curve at an average temperature of 375° between the wall and the center. Beyond this point the volatile constituents of the coal are distilled at a uniform rate, and the decomposition reactions become exothermic. In practice, this was evidenced by the necessity of reducing the heat input somewhat in order to keep the temperature constant. Hollings and Cobb[5] report a similar thermal effect in their work on the heat of carbonization of coal.

COLLECTION OF BY-PRODUCTS.

The apparatus used for the collection of the by-products was essentially the same as the one used by Davis and Berger[6]. Referring to Figure 2 for arrangement of this apparatus, the distillates were partly condensed in an air condenser *g*, from which they were conducted to a water condenser *h*, which served as a reservoir for all of the condensate. The uncondensed gases then passed through an electrostatic precipitator *i* of the Cottrell type, which removed the finely divided tar mists. The ammonia scrubber *j* contained 300 c.c. of 1:10 sulphuric acid. Any light uncondensed oils were removed from the gases by passing through the U-tube *k*, which was filled with activated charcoal. The clean fixed gases were then measured by the meter and stored in a large gas tank for later examination. This apparauts was suitable for complete collection of all of the by-products. The electrostatic precipitator gave a little trouble when the gases were being evolved at the maximum rate. During this time the tar vapors reached the top of the precipitator, and a small amount passed over into the ammonia scrubber; but this trouble was of short duration, so the errors caused thereby were small. The yield of liquid by-products was determined by weighing. For accurate yield of tar, the amount of water it contained was determined and deducted from the weight of tar emulsion; the specific gravity of dry tar was also determined, and from this and the corrected weight the volumetric yield could be calculated.

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[5] Hollings, Harold, and Cobb, J. W., A thermal study of the carbonization process: *Jour.* Chem. Soc., vol. 107, 1915, pp. 1106-1115.

[6] Work cited.

Ammonia.—For accurate estimation of the amount of ammonia liberated in the experiments, the sulphuric scrubber was standardized before and after carbonization, by titration. The amount of ammonia contined in the tar liquor was determined by distillation with caustic, in accordance with the usual method for the analysis of ammonia liquors[7].

Light oils.—Eight hundred grams of activated charcoal was sufficient to extract the light oils from the gas. At the end of a run the charcoal was steamed out at 500° in an electric retort, the light-oil vapors being condensed and collected in a cooled container. It required two hours to liberate the light oils and to renew the absorptive capacity of the charcoal. These recovered products represented only about 50 per cent by weight of the gain in weight of the charcoal, since a large amount of the vapors and gases absorbed by it would not condense at the temperature of tap water.

Collection and sampling of the gas.—All of the gas liberated in the process was stored in a large gasometer over water, where it stood for a few hours to allow for mixing after which samples were taken for analysis.

TABLE 2.—*Survey of yields from low-temperature coking of typical Pennsylvania coals at 550° C.*

Coal.	Tar dehydrated, gallons per ton.	Coke, per cent.	Gas, cu. ft. per ton.	Light oil, charcoal scrubber, gallons per ton.	Ammonium sulphate, pounds per ton.
Lower Freeport	27	71.0	3450	2.6	7.0
Upper Freeport	33	70.5	3400	2.8	7.0
Pittsburgh bed	35	70.0	3310	3.2	7.5
Pittsburgh roof, lower bench	24.6	73.2	2700	2.2	7.3
Pittsburgh roof, upper bench	22.3	73.8	2200	2.8	7.3
Pittsburgh rooster	25	74.8	2600	2.9	6.4
Upper Kittanning	4.3	90.0	1400	...	1.5

DISCUSSION OF RESULTS.

Figures 5, 6, 7, 8, and 9 give a complete survey of the yields obtained on carbonizing the various Pennsylvania coals, results being calculated to the basis of a one-ton charge of coal. Table 2 gives a comparative survey of the yields.

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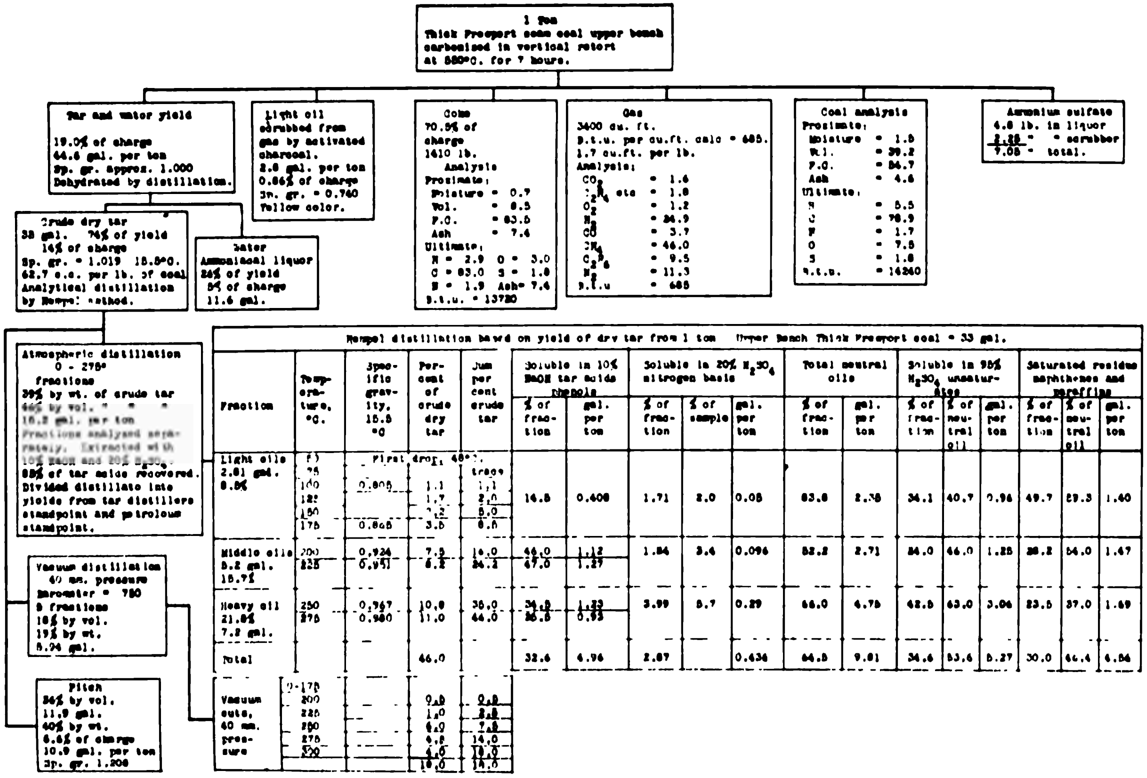
[7] Gas Chemists' Hand Book, 2nd ed., 1922, pp. 222-223.

COKE.

All of the coals used in the experiements produced strong coke, except the Kittanning. They are, in fact, among the best



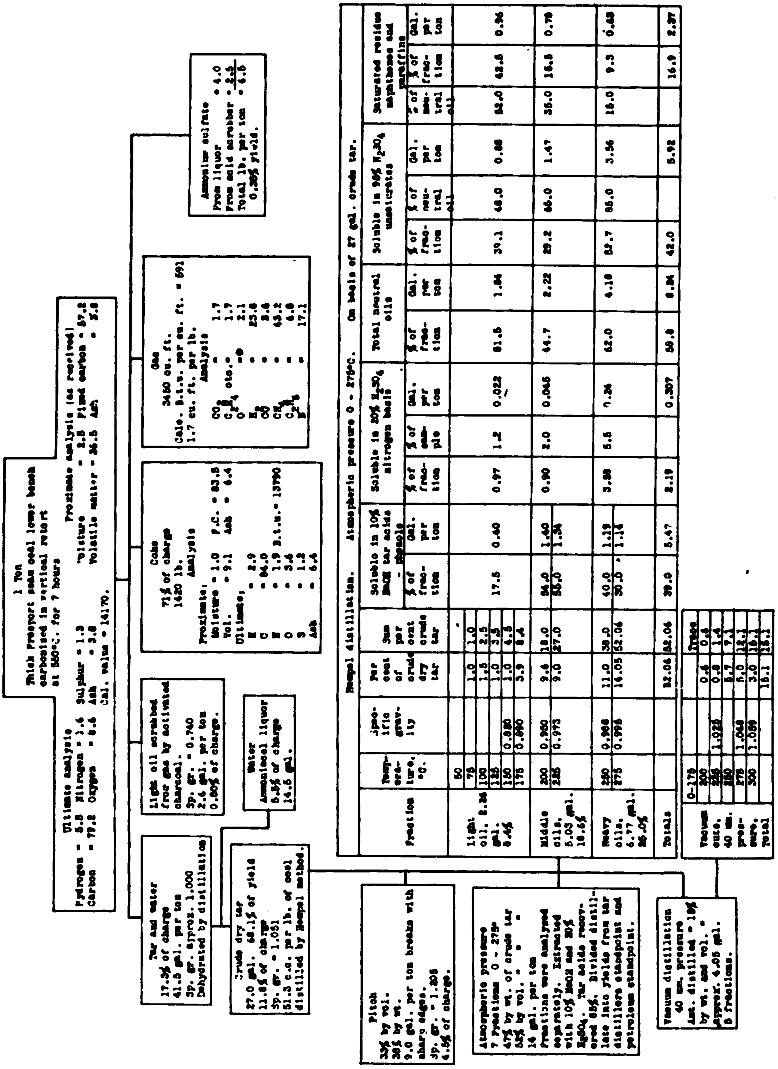
Hempel distillation based on yield of dry tar from 1 ton Upper Bench Thick Freeport coal = 33 gal.

Fraction	Temperature, °C.	Specific gravity, 15.5 °C	Per cent of crude dry tar	Sum per cent crude tar	Soluble in 10% NaOH tar acids phenols: % of fraction	Soluble in 10% NaOH tar acids phenols: gal. per ton	Soluble in 20% H_2SO_4 nitrogen basis: % of fraction	Soluble in 20% H_2SO_4 nitrogen basis: % of sample	Soluble in 20% H_2SO_4 nitrogen basis: gal. per ton	Total neutral oils: % of fraction	Total neutral oils: gal. per ton	Soluble in 98% H_2SO_4 unsaturates: % of fraction	Soluble in 98% H_2SO_4 unsaturates: % of neutral oil	Soluble in 98% H_2SO_4 unsaturates: gal. per ton	Saturated residue naphthenes and paraffins: % of fraction	Saturated residue naphthenes and paraffins: % of neutral oil	Saturated residue naphthenes and paraffins: gal. per ton
Light oils 2.81 gal. 8.5%	[illegible] 75 100 125 150 175	First drop, 48°C. 0.808 0.848	 1.1 1.7 2.2 3.5	 trace 1.1 2.8 5.0 8.5	14.5	0.408	1.71	2.0	0.05	63.8	2.38	34.1	40.7	0.96	49.7	29.3	1.40
Middle oils 5.2 gal. 15.7%	200 225	0.924 0.951	7.5 8.2	16.0 24.2	46.0 47.0	1.12 1.27	1.84	3.4	0.096	52.2	2.71	24.0	46.0	1.25	28.2	54.0	1.47
Heavy oil 21.8% 7.2 gal.	250 275	0.967 0.980	10.8 11.0	35.0 46.0	34.8 36.5	1.23 0.93	3.99	5.7	0.29	66.0	4.75	42.5	63.0	3.06	23.5	37.0	1.69
Total			46.0		32.6	4.96	2.87		0.434	64.5	9.81	34.6	53.6	5.27	30.0	64.4	4.84
Vacuum cuts, 40 mm. pressure	0-175 200 225 250 275 300		 2.0 1.0 4.8 6.2 4.0 18.0	 2.0 3.0 7.8 14.0 18.0 18.0													

FIGURE 5.—*Flow-sheet giving details of by-products from Thick Freeport bed, upper bench coal.*

coking coals in this country for high-temperature carbonization, so it is expected that they should form good low-temperature coke.

According to Lewes[8], for a coal to give a good coke it must be sufficiently fusible under the influence of heat or give enough liquid products of not too volatile a nature at low temperature to cause particles of residue to adhere. The fusion of this coking or resinous material takes place at about 350°. Upon further applica-



Hempel distillation. Atmospheric pressure 0 - 275°C. On basis of 27 gal. crude tar.

Fraction	Temperature, °C.	Specific gravity	Per cent of crude dry tar	Sum per cent crude tar	Soluble in 10% NaOH tar acids - phenols: % of fraction	Soluble in 10% NaOH tar acids - phenols: Gal. per ton	Soluble in 20% H_2SO_4 nitrogen basis: % of fraction	Soluble in 20% H_2SO_4 nitrogen basis: % of sample	Soluble in 20% H_2SO_4 nitrogen basis: Gal. per ton	Total neutral oils: % of fraction	Total neutral oils: Gal. per ton	Soluble in 98% H_2SO_4 unsaturates: % of fraction	Soluble in 98% H_2SO_4 unsaturates: % of neutral oil	Soluble in 98% H_2SO_4 unsaturates: Gal. per ton	Saturated residue naphthenes and paraffins: % of neutral oil	Saturated residue naphthenes and paraffins: % of fraction	Saturated residue naphthenes and paraffins: Gal. per ton
Light oil, 2.26 gal. 8.4%	50				17.5	0.40	0.97	1.2	0.022	81.5	1.84	39.1	48.0	0.88	52.0	42.5	0.96
	75		1.0	1.0													
	100		1.5	2.5													
	125		1.0	3.5													
	150	0.820	1.0	4.5													
	175	0.890	3.9	8.4													
Middle oils, 5.03 gal. 18.6%	200	0.950	9.6	18.0	54.0	1.40	0.90	2.0	0.046	44.7	2.22	29.2	66.0	1.47	35.0	16.5	0.78
	225	0.973	9.0	27.0	56.0	1.34											
Heavy oils, 6.77 gal. 26.0%	250	0.988	11.0	38.0	40.0	1.19	3.58	5.5	0.24	62.0	4.18	52.7	85.0	3.56	15.0	9.3	0.68
	275	0.998	14.05	52.06	30.0	1.14											
Totals			52.06	52.06	39.0	5.47	2.19		0.307	58.8	8.24	42.0		5.92		16.9	2.37

Vacuum cuts, 40 mm. pressure,	0-175			Trace
	200		0.6	0.6
	225	1.025	0.8	1.4
	250		5.7	7.1
	275	1.048	5.0	12.1
	300	1.059	3.0	15.1
Total			15.1	15.1

FIGURE 6.—*Flow-sheet giving details of by-products from Thick Freeport bed, lower bench coal.*

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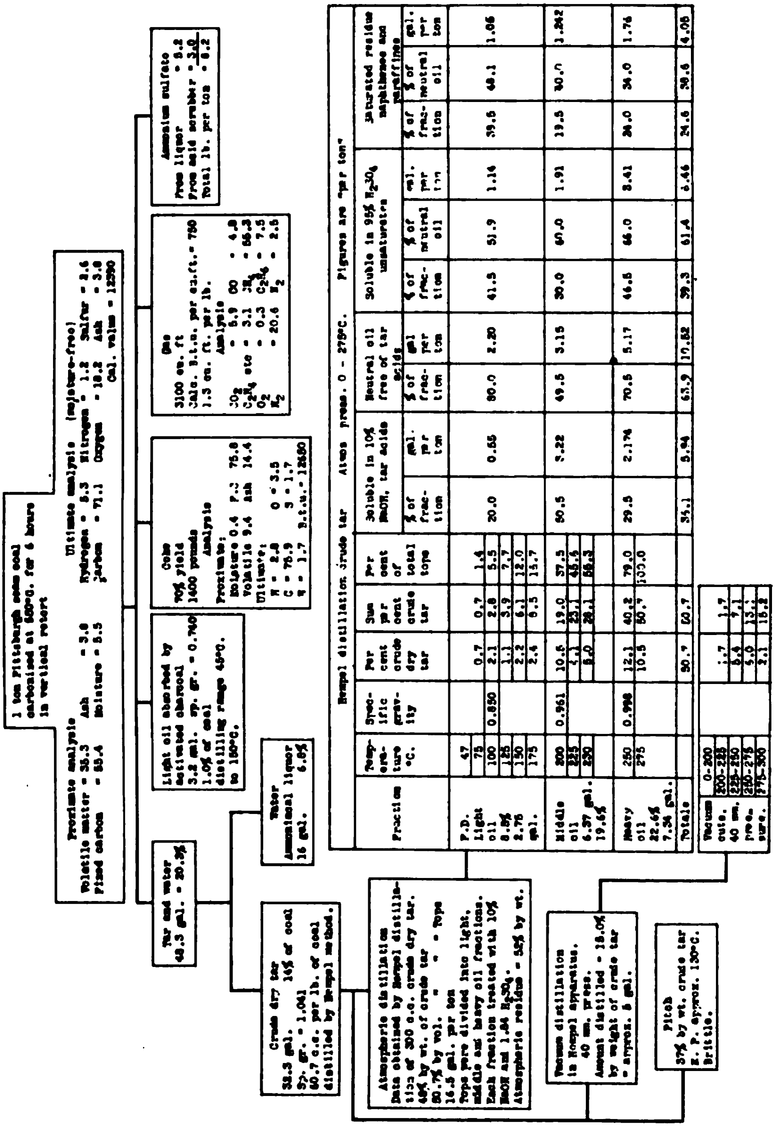
[8] Lewes, V. B., Carbonization of coal: edition of 1912, p. 210.

tion of heat it breaks up to form the liquid and gaseous by-products; the residue from the breaking-up is the binding material.



1 ton Pittsburgh seam coal carbonized at 550°C. for 6 hours in vertical retort

Proximate analysis
Volatile matter = 35.3 Ash = 3.8
Fixed carbon = 55.4 Moisture = 5.5

Ultimate analysis (moisture-free)
Hydrogen = 5.3 Nitrogen = 1.2 Sulfur = 2.6
Carbon = 71.1 Oxygen = 18.2 Ash = 3.8
Cal. value = 12390

Tar and water
48.3 gal. = 20.3%

Light oil absorbed by activated charcoal
3.2 gal. sp. gr. = 0.760
1.0% of coal
distilling range 45°C. to 150°C.

Coke
70% yield
1400 pounds
Analysis
Proximate:
Moisture 0.4 F.C. 75.8
Volatile 9.4 Ash 14.4
Ultimate:
H = 2.8 O = 3.5
C = 75.9 S = 1.7
N = 1.7 B.t.u. = 12680

Gas
3100 cu. ft
Calc. B.t.u. per cu.ft. = 750
1.3 cu. ft. per lb.
Analysis
CO_2 = 5.9 CO = 4.8
C_2H_4 etc = 3.1 CH_4 = 56.3
O_2 = 0.3 C_2H_6 = 7.5
H_2 = 20.6 N_2 = 2.5

Ammonium sulfate
From liquor = 5.2
From acid scrubber = 3.0
Total lb. per ton = 8.2

Crude dry tar
32.3 gal. 14% of coal
Sp. gr. = 1.041
60.7 c.c. per lb. of coal distilled by Hempel method.

Water
Ammoniacal liquor
16 gal. 6.8%

Atmospheric distillation
Data obtained by Hempel distillation of 300 c.c. crude dry tar.
48% by wt. of crude tar
50.7% by vol. " " " = Tops
16.5 gal. per ton
Tops were divided into light, middle and heavy oil fractions.
Each fraction treated with 10% NaOH and 1.84 H_2SO_4.
Atmospheric residue = 52% by wt.

Vacuum distillation in Hempel apparatus.
40 mm. press.
Amount distilled = 15.0% by weight of crude tar = approx. 5 gal.

Pitch
37% by wt. crude tar
M. P. approx. 130°C.
Brittle.

Hempel distillation crude tar Atmos press. 0 - 275°C. Figures are "per ton"

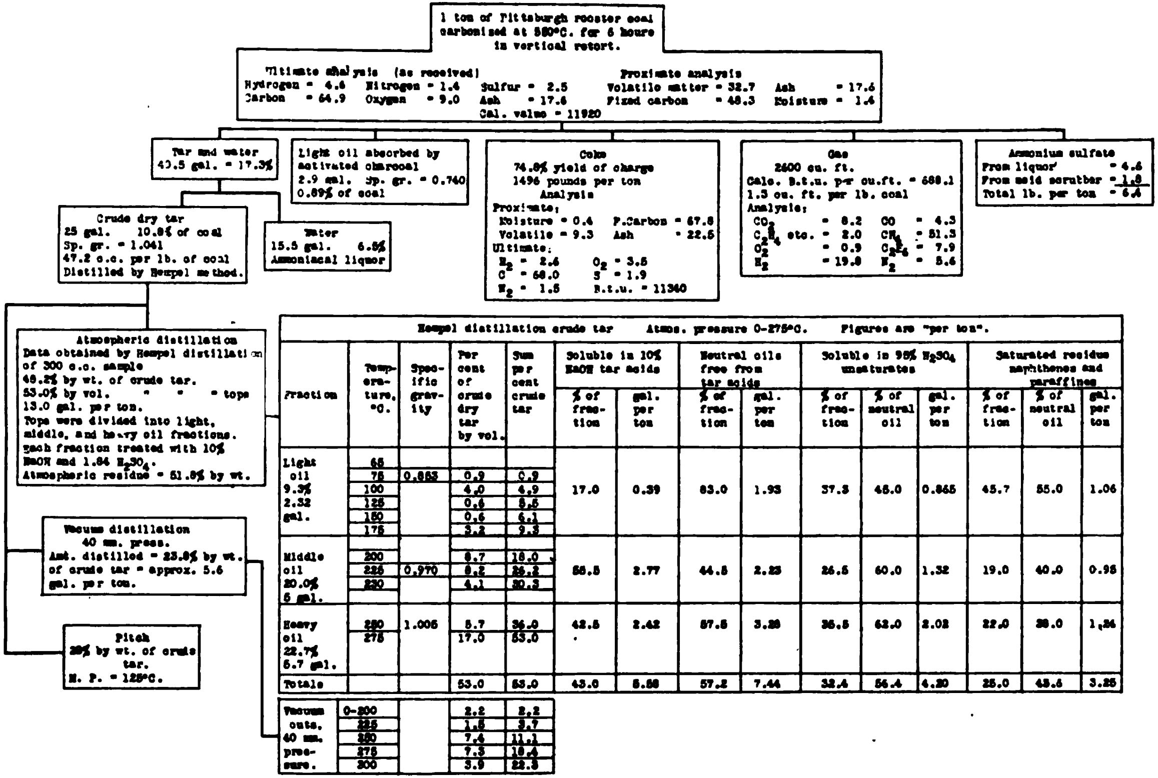
Fraction	Temperature °C.	Specific gravity	Per cent crude dry tar	Sum per cent crude tar	Per cent of total tops	Soluble in 10% NaOH, tar acids		Neutral oil free of tar acids		Soluble in 95% H_2SO_4 unsaturates			Saturated residue naphthenes and paraffines		
						% of fraction	gal. per ton	% of fraction	gal per ton	% of fraction	% of neutral oil	gal. per ton	% of fraction	% of neutral oil	gal. per ton
P.D. Light oil 8.5% 2.75 gal.	47					20.0	0.55	80.0	2.20	41.5	51.9	1.14	39.5	48.1	1.06
	75		0.7	0.7	1.4										
	100	0.850	2.1	2.8	5.5										
	125		1.1	3.9	7.7										
	150		2.2	6.1	12.0										
	175		2.4	8.5	15.7										
Middle oil 6.37 gal. 19.6%	200	0.961	10.5	19.0	37.5	50.5	3.22	49.5	3.15	30.0	60.0	1.91	19.5	40.0	1.242
	225		4.1	23.1	45.6										
	230		5.0	28.1	56.3										
Heavy oil 22.6% 7.34 gal.	250	0.998	12.1	40.2	79.0	29.5	2.174	70.5	5.17	46.5	66.0	3.41	24.0	34.0	1.76
	275		10.5	50.7	100.0										
Totals			50.7	50.7		35.1	5.94	63.9	10.52	39.3	61.4	6.46	24.6	38.6	4.08

Vacuum cuts. 40 mm. pressure.			Per cent crude dry tar	Sum per cent crude tar
	0-200			
	200-225		1.7	1.7
	225-250		5.4	7.1
	250-275		6.0	13.1
	275-300		2.1	15.2

FIGURE 7.—*Flow-sheet giving details of by-products from Pittsburgh bed coal.*

As proved by previous investigators, temperature and pressure have a marked influence upon the character of the coke produced.

Charpy and Decorps[9] concluded from their investigations that each coal possesses a marked individuality, and that it is imprudent



1 ton of Pittsburgh rooster coal
carbonized at 580°C. for 6 hours
in vertical retort.

Ultimate analysis (as received)
Hydrogen = 4.6 Nitrogen = 1.4 Sulfur = 2.5
Carbon = 64.9 Oxygen = 9.0 Ash = 17.6
Cal. value = 11920

Proximate analysis
Volatile matter = 32.7 Ash = 17.6
Fixed carbon = 48.3 Moisture = 1.4

Tar and water
40.5 gal. = 17.3%

Light oil absorbed by
activated charcoal
2.9 gal. Sp. gr. = 0.740
0.89% of coal

Coke
74.8% yield of charge
1496 pounds per ton
Analysis
Proximate;
Moisture = 0.4 F.Carbon = 67.8
Volatile = 9.3 Ash = 22.5
Ultimate:
H_2 = 2.6 O_2 = 3.5
C = 68.0 S = 1.9
N_2 = 1.5 B.t.u. = 11340

Gas
2600 cu. ft.
Calc. B.t.u. per cu.ft. = 688.1
1.3 cu. ft. per lb. coal
Analysis;
CO_2 = 8.2 CO = 4.3
C_2H_4 etc. = 2.0 CH_4 = 51.3
O_2 = 0.9 C_2H_6 = 7.9
H_2 = 19.8 N_2 = 5.6

Ammonium sulfate
From liquor = 4.6
From acid scrubber = 1.8
Total lb. per ton = 6.4

Crude dry tar
25 gal. 10.8% of coal
Sp. gr. = 1.041
47.2 c.c. per lb. of coal
Distilled by Hempel method.

Water
15.5 gal. 6.5%
Ammoniacal liquor

Atmospheric distillation
Data obtained by Hempel distillation
of 300 c.c. sample
48.2% by wt. of crude tar.
53.0% by vol. " " " = tops
13.0 gal. per ton.
Tops were divided into light,
middle, and heavy oil fractions.
Each fraction treated with 10%
NaOH and 1.84 H_2SO_4.
Atmospheric residue = 51.8% by wt.

Vacuum distillation
40 mm. press.
Amt. distilled = 23.8% by wt.
of crude tar = approx. 5.6
gal. per ton.

Pitch
28% by wt. of crude
tar.
M. P. = 125°C.

Hempel distillation crude tar Atmos. pressure 0-275°C. Figures are "per ton".

Fraction	Temperature, °C.	Specific gravity	Per cent of crude dry tar by vol.	Sum per cent crude tar	Soluble in 10% NaOH tar acids		Neutral oils free from tar acids		Soluble in 95% H_2SO_4 unsaturates			Saturated residue naphthenes and paraffines		
					% of fraction	gal. per ton	% of fraction	gal. per ton	% of fraction	% of neutral oil	gal. per ton	% of fraction	% of neutral oil	gal. per ton
Light oil 9.3% 2.32 gal.	65				17.0	0.39	83.0	1.93	37.3	45.0	0.865	45.7	55.0	1.06
	75	0.853	0.9	0.9										
	100		4.0	4.9										
	125		0.6	5.5										
	150		0.6	6.1										
	175		3.2	9.3										
Middle oil 20.0% 5 gal.					55.5	2.77	44.5	2.23	26.5	60.0	1.32	19.0	40.0	0.95
	200		8.7	18.0										
	225	0.970	8.2	26.2										
	250		4.1	30.3										
Heavy oil 22.7% 5.7 gal.	250	1.006	5.7	36.0	42.5	2.42	57.5	3.28	35.5	62.0	2.02	22.0	38.0	1.24
	275		17.0	53.0										
Totals			53.0	53.0	43.0	5.58	57.2	7.44	32.4	56.4	4.20	25.0	43.6	3.25
Vacuum cuts, 40 mm. pressure.	0-200		2.2	2.2										
	225		1.5	3.7										
	250		7.4	11.1										
	275		7.3	18.4										
	300		3.9	22.3										

FIGURE 8.—*Flow-sheet giving details of by-products from Pittsburgh roof coal.*

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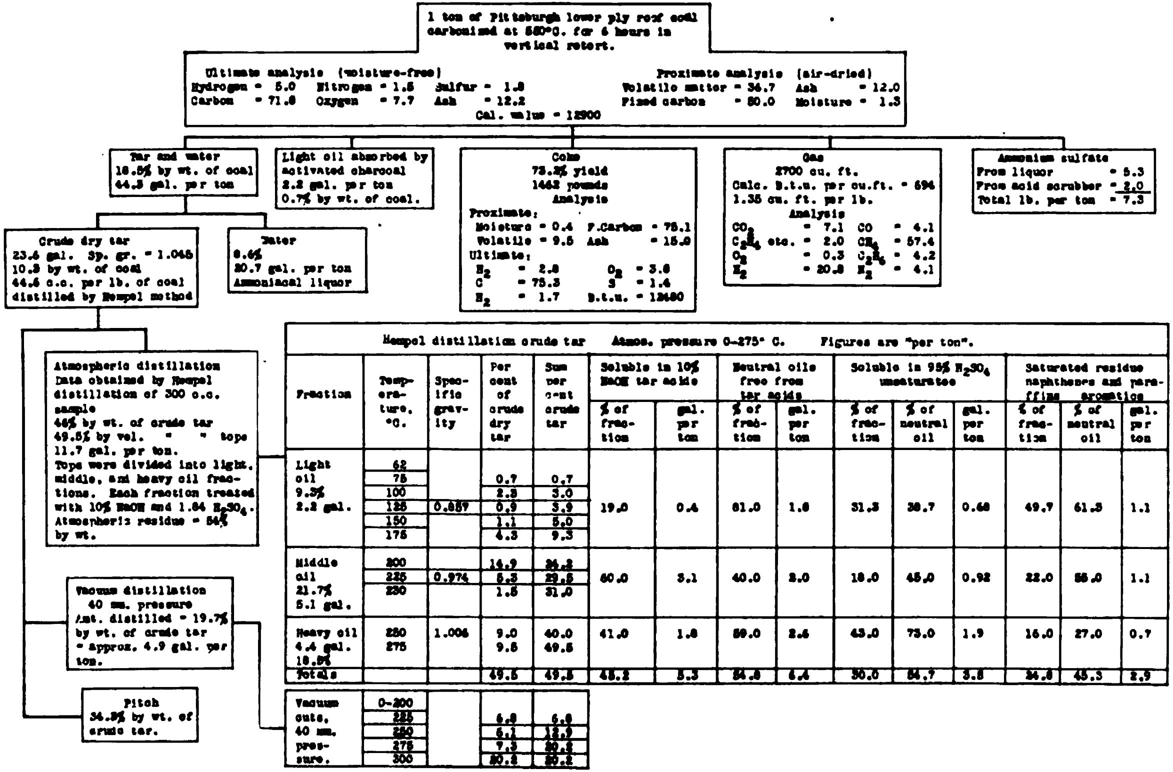
[9] Charpy, Georges, and Decorps, Gaston, The conditions of formation of coke: Compt. Rend., vol. 168, 1919, p. 1301.

to neglect experimentation to determine the conditions most favorable to coke formation—that there is no general criterion whereby the coking quality of coal may be judged. Suffice it to say that the



1 ton of Pittsburgh lower ply roof coal carbonized at 550°C. for 6 hours in vertical retort.

Ultimate analysis (moisture-free)
Hydrogen = 5.0 Nitrogen = 1.5 Sulfur = 1.8
Carbon = 71.8 Oxygen = 7.7 Ash = 12.2
Cal. value = 12900

Proximate analysis (air-dried)
Volatile matter = 36.7 Ash = 12.0
Fixed carbon = 50.0 Moisture = 1.3

Tar and water
18.5% by wt. of coal
44.5 gal. per ton

Light oil absorbed by activated charcoal
2.2 gal. per ton
0.7% by wt. of coal.

Coke
73.2% yield
1462 pounds
Analysis
Proximate:
Moisture = 0.4 F.Carbon = 75.1
Volatile = 9.5 Ash = 15.0
Ultimate:
H_2 = 2.8 O_2 = 3.8
C = 75.3 S = 1.4
N_2 = 1.7 B.t.u. = 12480

Gas
2700 cu. ft.
Calc. B.t.u. per cu.ft. = 694
1.35 cu. ft. per lb.
Analysis
CO_2 = 7.1 CO = 4.1
C_2H_4 etc. = 2.0 CH_4 = 57.4
O_2 = 0.3 C_2H_6 = 4.2
H_2 = 20.8 N_2 = 4.1

Ammonium sulfate
From liquor = 5.3
From acid scrubber = 2.0
Total lb. per ton = 7.3

Crude dry tar
23.6 gal. Sp. gr. = 1.045
10.3 by wt. of coal
44.6 c.c. per lb. of coal
distilled by Hempel method

Water
8.6%
20.7 gal. per ton
Ammoniacal liquor

Atmospheric distillation
Data obtained by Hempel distillation of 300 c.c. sample
46% by wt. of crude tar
49.5% by vol. " " tops
11.7 gal. per ton.
Tops were divided into light, middle, and heavy oil fractions. Each fraction treated with 10% NaOH and 1.84 H_2SO_4.
Atmospheric residue = 54% by wt.

Vacuum distillation
40 mm. pressure
Amt. distilled = 19.7% by wt. of crude tar
= approx. 4.9 gal. per ton.

Pitch
34.3% by wt. of crude tar.

Hempel distillation crude tar Atmos. pressure 0–275° C. Figures are "per ton".

Fraction	Temperature, °C.	Specific gravity	Per cent of crude dry tar	Sum per cent crude tar	Soluble in 10% NaOH tar acids: % of fraction	Soluble in 10% NaOH tar acids: gal. per ton	Neutral oils free from tar acids: % of fraction	Neutral oils free from tar acids: gal. per ton	Soluble in 95% H_2SO_4 unsaturates: % of fraction	Soluble in 95% H_2SO_4 unsaturates: % of neutral oil	Soluble in 95% H_2SO_4 unsaturates: gal. per ton	Saturated residue naphthenes and paraffins aromatics: % of fraction	Saturated residue naphthenes and paraffins aromatics: % of neutral oil	Saturated residue naphthenes and paraffins aromatics: gal. per ton
Light oil 9.3% 2.2 gal.	62													
	75		0.7	0.7										
	100		2.3	3.0										
	125	0.887	0.9	3.9	19.0	0.4	61.0	1.8	31.3	38.7	0.68	49.7	61.3	1.1
	150		1.1	5.0										
	175		4.3	9.3										
Middle oil 21.7% 5.1 gal.	200		14.9	24.2										
	225	0.974	5.3	29.5	60.0	3.1	40.0	2.0	18.0	45.0	0.92	22.0	55.0	1.1
	250		1.5	31.0										
Heavy oil 4.4 gal. 18.5%	250	1.006	9.0	40.0	41.0	1.8	59.0	2.6	43.0	73.0	1.9	16.0	27.0	0.7
	275		9.5	49.5										
Totals			49.5	49.5	45.2	5.3	54.8	6.4	30.0	54.7	3.5	34.8	45.3	2.9
Vacuum cuts, 40 mm. pressure.	0–200													
	225		6.8	6.8										
	250		6.1	12.9										
	275		7.3	20.2										
	300		20.2	20.2										

FIGURE 9.—*Flow-sheet giving details of by-products from Pittsburgh roof coal, lower ply.*

coals used in this investigation, with the exception of the Kittanning, produced good cokes of fairly dense structure, which seem to be well suited for domestic use as a substitute for anthracite. They were cemented throughout, and a small proportion of fines was produced in discharging from the retort. Figure 10 shows a representative coke obtained from the experiments, and Table 3 gives

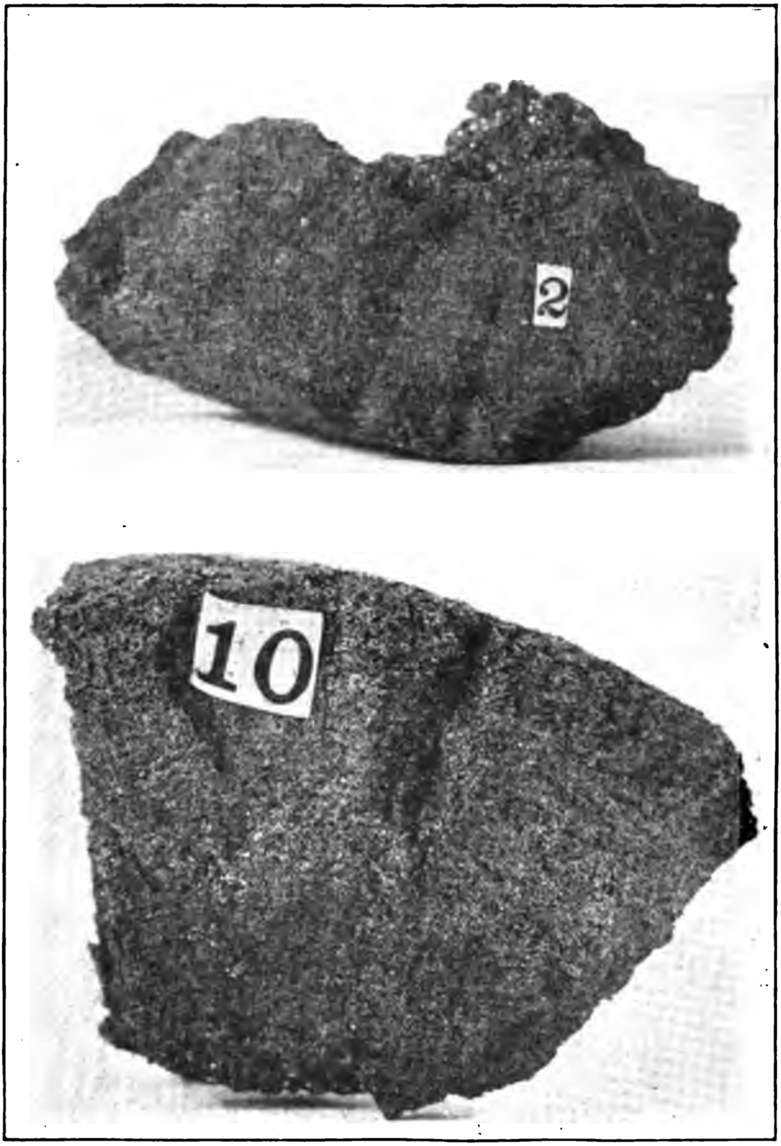


Figure 10.—*Representative coke obtained by carbonizing Freeport coal—No. 2 at 550° C., and No. 10 at 600 to 650 C.*

the analysis of all cokes made. All were similar in structure, and also similar as regards volatile matter and fixed carbon ratio. This is shown in Table 4.

TABLE 4.—*Volatile matter and fixed carbon ration of coal and coke.*

Coal.	Before carbonizing.	After carbonizing.
Lower Freeport	1.6	9.2
Upper Freeport	1.4	9.7
Pittsburgh bed	1.4	7.5
Pittsburgh rooster	1.5	7.3
Pittsburgh lower roof	1.4	7.9
Pittsburgh upper roof	1.4	7.6
Upper Kittanning	4.2	10.2

In their distillation of similar coals at 600 to 650°, Davis and Berger[10] obtained coke of 2 to 3 per cent of volatile matter. The investigations of the same type of coals at 550° yielded a coke of 9 to 10 per cent volatile matter. This shows that a variation of the temperature of carbonization approximating 60° has a marked effect upon the volatile content of the coke residue. Cokes produced at 600 to 650° show a very small difference in physical structure from those coked at 550°, and to all appearances they are the same. Above 600° it begins to assume the requirements for metallurgical coke; that produced at about 550° would be more free-burning and therefore better suited for domestic use.

Regarding the efficiacy of low-temperature coke in domestic appliances, Fishenden[11] shows that the coke has a superiority over coal. To quote:

> Various types of grates and cooking apparatus were used. Comparisons were made between a soft caking bituminous coal of 14700 B. t. u. and 3.2 per cent ash, and a low-temperature coke made at the Fuel Research Board's station of 11900 to 13200 B. t. u. with ash content of 8.8 to 12 per cent.
>
> The results of the test show that low-temperature coke has a limited superiority over coal in the matter of radiant efficiency, but with the price of coke higher than the price of coal there seems to be no attraction for its use except as a smokeless fuel.

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[10] Work cited.

[11] Fishenden, Margaret W., Efficiency of low-temperature coke in domestic appliances: Tech. Paper 3, Fuel Research Board, *Jour.* Soc. Chem. Ind., vol. 41, 1921, pp. 13-14.

TABLE 3.—*Analyses of cokes produced.*

Bed and Place.	Proximate Analysis				Ultimate Analysis.				
	Moisture.	Volatile matter.	Fixed carbon.	Ash.	Hydrogen.	Carbon.	Nitrogen.	Oxygen.	Sulphur.
Pittsburgh bed, Burgettstown, Pa.	(a) 0.4	9.4	75.8	14.4	2.8	75.9	1.7	3.5	1.7
	(b) ...	11.1	83.9	....	3.3	89.0	2.0	3.7	2.0
	(c) 4.6	35.4	49.5	10.5	5.4	69.1	1.3	11.1	2.6
Pittsburgh rooster coal, Burgettstown, Pa.	(a) 0.4	9.3	67.8	22.5	2.6	68.0	1.5	3.5	1.9
	(b) ...	12.1	87.9	....	3.3	88.2	2.0	4.0	2.5
	(c) 1.4	32.7	48.3	17.6	4.6	64.9	1.4	9.0	2.5
Pittsburgh roof coke, upper ply	(a) 0.3	8.3	63.0	28.4	...	....	...	...	...
	(b) ...	11.7	88.8	....	...	....	...	...	...
	(c) 2.6	31.1	43.7	22.6	...	....	...	...	...
Pittsburgh roof coke, lower ply	(a) 0.4	9.5	75.1	15.0	2.8	75.3	1.7	3.8	1.4
	(b) ...	11.2	88.8	....	3.2	89.0	2.0	4.1	1.7
	(c) 3.2	35.9	49.1	11.8	5.2	69.5	1.4	10.3	1.8
Freeport coke, upper bench, Curtisville, Pa.	(a) 0.7	8.5	83.4	7.4	2.8	83.0	1.9	3.0	1.8
	(b) ...	9.3	91.7	....	3.0	90.3	2.0	2.7	2.0
	(c) 1.5	39.2	54.7	4.6	5.5	78.9	1.7	7.5	1.8
Freeport coke, lower bench, Curtisville, Pa.	(a) 1.0	9.1	83.5	6.4	2.9	84.0	1.9	3.6	1.2
	(b) ...	9.9	90.1	....	3.0	90.7	2.1	3.0	1.2
	(c) 2.5	36.5	57.2	3.8	5.5	79.2	1.6	8.6	1.3
Upper Kittanning, Jerome, Pa.	(a) 0.1	8.4	85.5	6.0	...	....	...	...	1.3
	(b) ...	8.9	91.1	....	...	....	...	...	1.3
	(c) 0.1	18.3	76.1	5.5	...	....	...	...	1.3

(a) Coke as received.
(b) Coke moisture and ash free.
(c) Original coal.
NOTE—*Specific apparent gravity of above coke averaged 0.690.*

THE SMOKELESS FUEL QUESTION.

Much has been said in favor of low-temperature coke as a solution of the smoke problem, and if all small consumers would adopt this fuel the writers believe that such claims would hold good. In the interest of smoke abatement[1a] it is not necessary for large consumers to use coke, excepting perhaps the railroads, and further, it may be questioned on good grounds whether this course will ever be economically feasible. Large power-plants can and do burn bituminous coal with little smoke and with high efficiency; it is only the small power user, who does not realize that smoke means waste, also the domestic consumer, that really require a smokeless fuel. Here indeed would seem to lie the legitimate field for low-temperature coke; but it must have something to recommend it besides its smokeless qualities in order that it may be made to bear a reasonable part of the process costs. It must command a higher price than competing fuels, and to this end it must be more economical, or more convenient to use, or both. So far this has not been demonstrated industrially; on the other hand, no one can deny the possibility of such success in the future. Laboratory experiments, such as this bulletin covers, can only give indication of carbonization conditions which will produce a suitable fuel; the economic phases of the question must be answered through demand on the part of the consumers. Obviously, a lasting demand can not be created or maintained through unsupported statements appearing in the technical literature.

SWELLING OF THE COKE.

One of the chief difficulties encountered in making coke at low temperatures arises from swelling of the charge, which does not contract again within the low-temperature range. In aggravated cases the product is friable and porous; furthermore, it sticks in the retort and is difficult to discharge. Some coals are worse than others in this respect, depending, according to Illingworth[1aa], on the amount and character of "resinic" or cementing compounds, and somewhat on the coking rate as well. Apparently, and this seems quite reasonable, objectionable swelling of the coke will take place when the constituents of the coal or conditions of carbonization are such that the coking mass is very viscous at the time of maximum elimination of the volatile matter. This causes large bubbles of vapor and gases to form under considerable pressure within the

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[1a] Smoke abatement, by Osborn Monnett: Tech. Paper 273, Bureau of Mines, 1923, pp. 12-21.

[1aa] Illingworth, S. Roy, Low-temperature carbonization of coal: Proc. South Wales Inst. Eng., vol. 38, 1923, p. 159.

Illingworth, S. Roy, The action of solvents on coal: *Fuel*, Nov. 24, 1922, p. 213.

TABLE 5.—*Analyses of gases from certain coals.*

Gas.	Lower Freeport.	Upper Freeport.	Pittsburgh bed seam.	Pittsburgh rooster coal.	Pittsburgh roof, upper ply.	Pittsburgh roof, lower ply.	Upper Kittanning.	Gas from Clairton by-product coking plant.[a]	Steam distillation of Freeport coal at 550°.
CO_2	1.6	2.2	6.1	8.2	7.1	8.1	2.5	1.8	4.2
C_2H_4, etc.	1.8	2.3	4.5	2.0	2.0	2.1	0.5	3.0	2.3
O_2	1.2	0.8	0.7	0.9	0.3	0.9	3.1	......	0.7
H_2	24.9	28.1	23.3	19.8	20.8	17.6	22.7	53.9	36.1
CO	3.7	4.1	4.6	4.3	4.1	4.1	1.0	3.5	5.2
CH_4	46.0	47.1	46.9	51.3	57.4	55.3	55.0	36.6	36.6
C_2H_6	9.5	7.8	10.8	7.9	4.2	8.0	0.0	......	5.9
N_2	11.3	7.6	3.1	5.6	4.1	3.9	5.2	3.2	9.0
B. t. u. per cu. ft., calculated	685.5	683	752	688	694	......	576	582.9	582
Yield, cu. ft. per ton	3450	3400	3310	2600	2200	2700	1400	12000	4100

[a] *By-product coke plant at Clairton, Pa. (F. F. Marquard.)*

mass, and when these break the charge is not plastic enough to cause the bubble walls to flow together. The result is a coke with large pores. None of the coals treated by the authors gave porous cokes, and no difficulty was experienced in discharging these from the retort; in every case there was some space between the finished charge and the retort walls. Taking this into consideration, however, and a central void as well, the coke occupied about 16 per cent more space in retort than the coal used. This figure was calculated by measuring the coke before it was broken up. A rough check on the result was obtained by reducing a portion of the coke to the same size as that of the coal used, and noting the relative volumes occupied by equal weights of the two; since the weight of coke produced from all of the coal charged was known, the amount of expansion could be estimated.

GAS.

Table 5 shows the analyses of gases obtained from the several coals on carbonization at 550°. An analysis of a typical high-temperature gas and that of a gas obtained by steam distillation at 550° are included for the purpose of comparison.

The low-temperature gases show characteristics to be expected of such gases—that is, the percentages of CH_4 and C_2H_6 are high, while the hydrogen is low, when the quantities of these constituents in high-temperature gas are considered as a basis of comparison. As a result, the heating values of gases obtained at 550° are high. Their yield, however, is low—not over 3,500 cubic feet per ton of coal carbonized. The gas from the steam-distilled charge differs slightly from the other low-temperature gases; its hydrogen content is high and the CH_4 is low. It was at first thought that the excess hydrogen might be accounted for through possible local overheating of the steam in the super-heater, but this would require that the oxides of carbon be high, which is not noticeably the case. Another possibility is the water-gas reaction. This, however, would require considerably higher retort temperatures than those observed, and besides this, carbon monoxide would be formed in quantity. In so far as the high figure for hydrogen may be considered significant it would seem that at this carbonization temperature, steam actually favors de-hydrogenation.

It is interesting to note the differences brought about in composition and yield of gases from a given coal merely by changing the carbonization temperature by 50 to 75°. This is shown in a striking manner in the following comparison (Table 6):

TABLE 6.—*Effect of slight variation of temperature on the quantity and quality of the gas evolved.*

Temperature, °C.	Yield.	Analysis.		
		Hydrogen.	Methane.	Ethane.
550	3400	28.1	47.1	7.8
600—650[a]	7175	47.2	33.7	4.4

[a] *Davis, J. D., and Berger, H. C., work cited.*

Evidently the temperatures of 550 to 650° are within the range where coal is extremely sensitive to temperature. In the available data on high-temperature carbonization, so large a variation in gas composition corresponding to small variations in carbonization temperatures is not mentioned.

AMMONIA.

According to Lewes[13], the larger part of the recoverable ammonia in coal is evolved at temperatures of 350 to 400°, but it continues to be evolved up to 600°, the amount obtained for any temperature depending somewhat upon the kind of coal used, the time of exposure of the ammonia gas to higher temperature, and also on the kind of material with which it comes in contact. The total amount recoverable evidently is not proportional to the total nitrogen of the coal, which varies within the narrow limits 1.2 to 2.0 per cent, but depends rather upon the manner in which it is combined in the coal. This last phase is a subject on which there is little information. It is known, however, that only 13 to 16 per cent of the total nitrogen of the coal is recovered by industrial methods of carbonization, and that the larger part of the remaining nitrogen is held so tenaciously that it can not be completely removed without destroying the coke. Steaming during carbonization recovers a part of the nitrogen as NH_3, water-gas being produced at the same time, while treatment with hydrogen at high temperature also converts some of the nitrogen to NH_3.

In view of what has been said, the ammonium sulphate yield of 5 to 8 obtained in these experiments seems to be of the order to be expected. Following are the results obtained by other experimenters, with carbonization conditions noted when available.

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[13] Work cited, p. 255.

TABLE 7.—*Yield of ammonium sulphate, as reported by certain investigators.*

Name.	Coal.	Process.[e]	Temperature, °C.	Yield of ammonium sulphate per ton of coal, pounds.
Curtis[a]	Clinchfield	Carbocoal—first stage	500	5 to 10
Armstrong[b]	Bernsley	Coalite	650	15 to 20
Davis and Berger[c]	Freeport	Laboratory scale—vertical retort	600-650	15 to 20
Lewes[d]	....	....	500	12

[a] Curtis, H. E., Chapman, W. E., Geldard, W. J., and Doughton, E. E., Low-temperature carbonization of coal: *Chem. & Met. Eng.*, vol. 28, 1923, pp. 11-17; 60-62; 118-123.

[b] Armstrong, H. L., Low-temperature carbonization: *Chem. Tr. Jour.*, vol. 67, 1920, p. 736.

[c] Work cited, p. 24.

[d] Work cited, p. 193.

[e] In none of the above cases was steaming resorted to.

EXAMINATION AND EVALUATION OF TAR OBTAINED BY CARBONIZING PENNSYLVANIA COALS AT 550° C.

Tar and water were collected in a water-cooled trap *b*, as shown in Figure 2. The water did not separate from the tar in a clean-cut layer, but about 50 per cent of it could be removed by a pipette. That which remained was emulsified in the tar, from which it could only be separated by distillation.

DEHYDRATION.

The best practical method found for removal of the water from the emulsion was by careful distillation at 120°. A large 2-gallon copper still was found convenient for this purpose; the total sample of tar, usually about 1400 c.c., being dehydrated in one operation by placing the still and contents inside of a constant temperature oven to ensure uniform heating. Owing to the large space above the liquid no trouble was experienced from "bumping." Water and light oils escaped through a small glass tube at the top of the retort, passed through an ice-packed condenser outside the oven, and were collected in a 200-c.c. graduated cylinder. Four hours at 120° was required to dehydrate the tar sufficiently for analytical distillation, after which the light oils that distilled in the process were pipetted from the water and returned to the cooled tar. The original content of water was determined by the method of Dean and Stark[14].

The specific gravity of the crude dry tar was determined with a pycnometer bottle of the Gay-Lussac type. The figures found varied from 1.040 to 1.065, which agree well with those usually found for low-temperature tars.

PLAN FOR EVALUATION OF LOW-TEMPERATURE OILS.

At the present time, low-temperature tar has no industrial consumption outside of its use as a fuel oil. There are few large plants operating in the low-temperature field, so standard methods of analysis of the tars obtained have not been developed, notwithstanding the quality of work that has been done on the chemical composition of such tars by numerous investigators[15]. These men have been interested mostly from a chemical rather than an engineering standpoint, and have applied their results in support of theories as to the constitution of coal and its behavior on heating.

Low-temperature tar produced below 700° differs materially from the high-temperature product. The tars obtained in the experimental work at 550° were brownish-black oils, fluid at room temperature, but more viscous than crude Pennsylvania petroleum. According to the many investigators, the principal characteristics of these tars are about the same . Lewes[16] states that they consist chiefly of hydrocarbons of the paraffin series, small quantities of aromatic hydrocarbons, and a large amount of the higher tar acids. This tar approaches the characteristics of crude petroleum and shale oil, so some of the methods used in the petroleum industry can be applied for its evaluation. A comparison of the boiling ranges of tar, shale oil, and petroleum, is given in Figure 11. It seems probable that an important use of low-temperature tar will be the relief of any petroleum shortage in the future, so the writers make a point of applying such tests to the tar as would classify it in a comparative way with petroleum. Only such tests were applied as would separate the principal products. Following is an outline of the scheme of analysis employed:

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[14] Dean, E. W., and Stark, D. D., Methods for testing petroleum products: Tech. Paper 298, Bureau of Mines, 1922, p. 35.

[15] Fischer, Franz, and Gluud, W.: Ges. Abhandl zur Kenntnis der Kohl, vol. 1, 1916, p. 114; Ber. vol. 52, 1919, p. 1035; see also Gas Abhandl, vol. 3, 1918, pp. 248-270.

Jones, D. T., and Wheeler, R. V., The composition of coal: *Jour.* Chem. Soc., vol. 105, 1914, p. 140.

Pictet, A., *Ann. Chim.* (9), vol. 10, 1918, p. 249.

Morgan, J. J., and Soule, R. P., Studies in carbonization of coal: *Chem. and Met. Eng.*, vol. 26, 1922, pp. 923-928; 977-981; 1025-1033.

Parr, S. W., and Olin, H. L., The coking of coal at low temperatures, with a preliminary study of by-products: Bull. 60, Univ. of Ill. Exp. Station, 1912. Also, The coking of coal at low temperatures, with special reference to the properties and composition of the products: Bull. 79, 1915, p. 20.

[16] Work cited, p. 202.

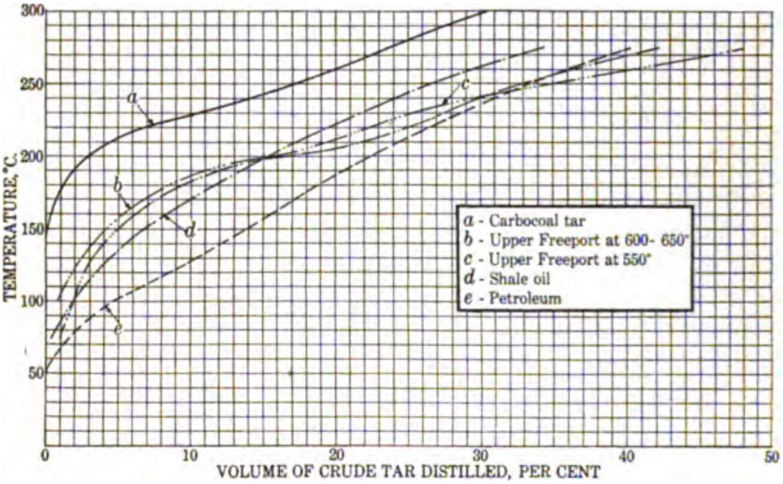

FIGURE 11.—*Distillation of crude oils and tars by Hempel method.*

Crude tar plus water.
- I. Dehydration.
  - A. Water.
    - (a) Ammonia.
  - B. Tar.
    - (a) Specific gravity.
    - (b) Hempel analytical distillation.
      - 1. Light oil, 0 to 175° C.
        - (a) Five fractions—specific gravity, unsaturation and content of tar acids determined. Boiling range of neutral oil.
      - 2. Middle oil, 175 to 225° C.
        - (a) Two fractions—specific gravity, unsaturation and content of tar acids determined. Boiling range of neutral oil.
      - 3. Heavy oil, 225 to 275° C.
        - (a) Two fractions—same determinations as under 2.
    - (c) Hempel distillation in vacuo at 40-mm. pressure.
      - 1. Fractions taken every 25 degrees.
        - (a) Specific gravity.
        - (b) Melting point.
    - (d) Pitch.
      - 1. Per cent by weight.
      - 2. Proximate analysis.
      - 3. Melting point.

For fractionation analysis of the crude tars the Hempel method was used, as described[17] in Bulletin 207 of the Bureau of Mines. The procedure given therein was rigidly followed. The curves given in Figure 12 show the boiling ranges of the various tars, plotted to the same scale. It will be noted that all of the tars have nearly the same volatility except that from the rooster coal of the Pittsburgh seam, which contained considerably more light oils boiling under 100° than others of the series. This particular light oil contained less phenols and unsaturates than the others. Probably the low-boiling constituents were naphthenes or benzene; but this could not be verified, since there was not sufficient sample for a complete analysis of the light oil. Reinhardt Thiessen of the Pittsburgh Experiment Station suggested to the writers that since the rooster coal contains more spore matter than other parts of the bed, we might expect to find the tars differing from the others. Davis and Berger[18] found that the cannel coals of the Thick Freeport bed, which is rich in spore matter, also give a high yield of light oils. Therefore, this may be taken as evidence indicating that the spore matter in coal contributes materially to yields of light oil.

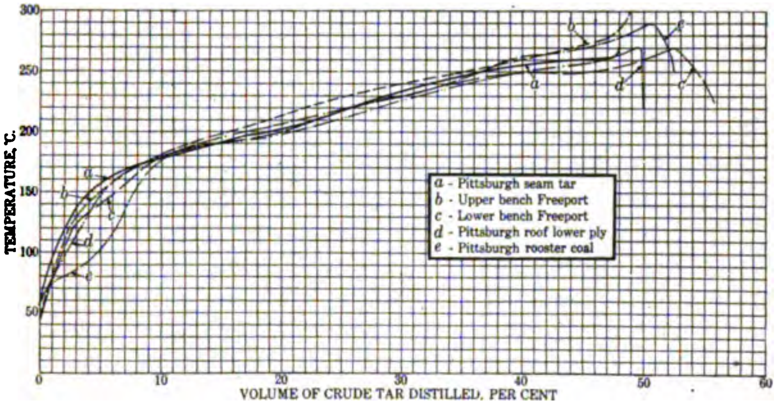

FIGURE 12.—*Hempel distillation of low-temperature tars at atmospheric pressure.*

Specific gravities of the "tops"—that is, oils boiling under 275° C.—were determined by means of the Westphal balance, all gravities being taken at 15.5°. The following shows the variation of the specific gravity with the boiling point of the fractions:

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[17] Dean, E. W., Hill, H. H., Smith, N. A. C., and Jacobs, W. A., The analytical distillation of petroleum and its products: Bull. 207, Bureau of Mines, 1922, p. 82.

[18] Work cited.

Boiling point, °C.	Specific gravity.
0-150	0.809
175	0.882
200	0.950
225	0.972
250	0.986
275	0.992

The cuts from the Hempel analysis were divided into three fractions according to the tars distillers' classification—namely, light oil, 0 to 175°; middle oil, 175 to 225°; and heavy oil, 225 to 275°. Each cut was treated with 10 per cent of sodium hydroxide for removal of the tar acids, for which purpose the Barrett separatory funnel was used. Twenty cubic centimeters of the oil to be tested was repeatedly agitated with the caustic until there was no discoloration in the liquor drawn off. The reduction in volume of the oil gave the volume of tar acids present. The nitrogen bases were next determined by repeated treatment of the phenol-free oil in the same separatory funnel with 20 per cent sulphuric acid. The residue remaining consisted of neutral oils.

The neutral oil was then treated to remove the unsaturated bodies by washing with 95 per cent sulphuric acid. This is an entirely empirical test, and must not be understood to effect a true separation of all unsaturated hydrocarbons from the oil. It does, however, give results comparable with those obtained in refining oil with sulphuric acid, and it therefore furnishes a fair means of comparing similar petroleum, shale, and tar oils. The Barrett funnel was used for this test also. The oil was agitated repeatedly until there was no reduction in volume, allowed to settle, after which the reduction in volume was read. The remaining oil included naphthene, paraffin, and aromatic hydrocarbons. Specific-gravity determinations were made on these fractions, and the results obtained averaged as follows: light oil, 0.803; middle oil, 0.861; and heavy oil, 0.928. The regular methods outlined[19] in Technical Paper 298 of the Bureau of Mines can be applied for further examination of the saturated residues. The residues remaining, however, from this series of tar oils were not of sufficient quantity for further investigation.

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[19] Methods for testing petroleum products: a handbook for inspecting laboratories: Tech. Paper 298, Bureau of Mines, 1922, 58 pp.

TAR ACIDS.

All investigators of low-temperature tar have reported high percentages of tar acids, and the tars obtained in this investigation were characteristic. Figure 13 shows the distribution of the tar acids from Freeport tar. It will be noted that the maximum content appears in the fraction boiling between 200 to 225°. In their work on the low-temperature tar from the Carbocoal process, Morgan and Soule[20] report similar appearance of the higher phenols; but their maximum content appears in the fraction boiling from 250 to 275°. Figures 5 to 9, inclusive, give the amount of tar acids obtained in the low-temperature carbonization of Pennsylvania coals.

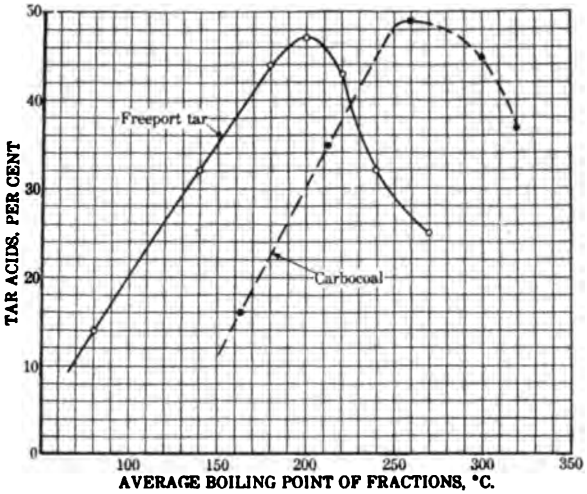

FIGURE 13.—*Tar acids in low-temperature tars.*

The tar acids were removed from the tops of a large-scale (4 kilograms) Hempel distillation of Freeport tar. Specific gravities and boiling ranges were determined for the acids separated from the light, middle, and heavy oil fractions, and were found to be 1.021; 1.028; and 1.052, respectively.

The boiling ranges were determined by the method of the Bureau of Mines for testing gasoline and kerosene. This method[21] is described in Bulletin 298. The tar acids from the middle fraction contained 70 per cent distilling between 195 and 210°, indicating predominance of cresols and xylenols. The curve for distillation of the tar acids from the heavy oil had a uniform slope, indicating no preponderance of any phenolic compound between 220 and 300 degrees.

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[20] Morgan, J. J., and Soule, R. P., Studies in the carbonization of coal: Bull. 8, Columbia University.

[21] Work cited.

The high yield (approximately 6 gal. per ton) of tar acids from low-temperature carbonization offers an interesting field of research. For profitable operation of low-temperature coking these compounds must have a market. At present the major part of the phenolic compounds derived from by-product coking serve as disinfectants and preservatives, but possibly by reduction of these phenols into benzol and homologues they could be utilized as motor fuels.

UNSATURATED MATERIAL IN THE TAR.

The unsaturated material removed by concentrated sulphuric acid is of no value at present, as judged by petroleum refining standards, and it goes into the refining loss. By the methods previously referred to, the neutral oil showed an increase in unsaturation with the boiling range; the presence of this material in the fractions was found to be approximately as follows: light oil, 42 per cent; middle oil, 45 per cent; and heavy oil, 63 per cent. These results indicate that there would be smaller refining loss in the lower boiling fraction, thus increasing profits in recovery of motor-fuel.

NITROGEN BASES.

The amount of nitrogen bases was estimated by washing the oil with 20 per cent sulphuric acid in a Barrett separatory funnel after removing the tar acids. These bases are only present in small amounts; Figure 14 shows their distribution. No attempt was made to study them on account of the small quantity recovered; however, a distinct odor of pyridine was noted therein. Most investigators have ignored nitrogen bases entirely. Morgan and Soule[22] have made a thorough investigation of their chemical and physical characteristics, and found that the pitch contains a greater quantity of these compounds than the distillate. Primary bases are only present in negligible quantities, secondary bases up to about 20 per cent, and tertiary bases up to 80 per cent.

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[22] Work cited.

INVESTIGATION OF THE EFFECTS OF SUPERHEATED STEAM ON THE YIELD AND QUALITY OF THE BY-PRODUCTS IN THE LOW-TEMPERATURE CARBONIZATION OF FREEPORT COAL.

Various claims have been made, notably by German writers[23], concerning the virtue of carbonizing coal at low temperatures in a current of superheated steam. The method is said to effect removal of the tar vapors from the retort as soon as they are formed, thus greatly minimizing secondary decomposition; a high yield of tar of superior quality is presumed to result from the treatment. Theoretically, these ideas seemed reasonable, and accordingly, a series of runs in superheated steam were made by the writers of this bulletin in order to find the advantages, if any, this method might possess over that previously employed. In carbonizing with steam it has usually been the practice to agitate the coking charge, thereby securing intimate contact with the steam. Doubtless the greatest possible effect of the steam is secured in this manner, but since it was desired that results of the steaming experiments be strictly comparable with previous tests, the additional variable involved in agitation was not introduced. In low-temperature carbonization, progress can best be realized when the many variable involved are dealt with singly.

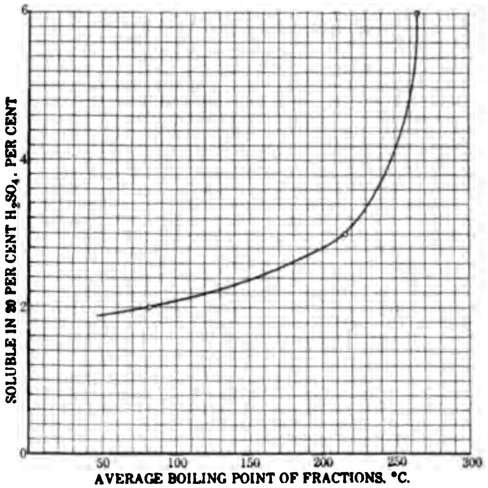

FIGURE 14.—*Nitrogen bases in neutral oil from low-temperature tar.*

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[23] Gluud, W., Tieftemperaturverkokung der Steinkohle: Verlag von Wilhelm Knapp, Halle, 1921.
Fischer, Franz, and Gluud, W., Untersuchung der deutschen Steinkohlen auf ihr Verhalten bei der T-verkokung: Ges. Abhandlg. zur Kennt. der Kohle, Bd. 3-S, 1918, p. 14.

APPARATUS.

Figure 15 is a diagrammatic representation of the apparatus used in these experiments. The arrangement is the same as that used in other experiments (See Figure 2), except that the condensing equipment was altered to provide greater cooling capacity, while apparatus for supplying superheated steam was added. In Figure 15, *g* is a water-cooled condenser, made of galvanized iron; *h* is a trap for collecting tar and water, and *f* is a 10-gallon steam boiler insulated by asbestos covering. At *t* is shown a union containing an orifice for regulating the flow of steam, and *e* is a superheating coil; *r* is a thermocouple for measuring the temperature of superheated steam.

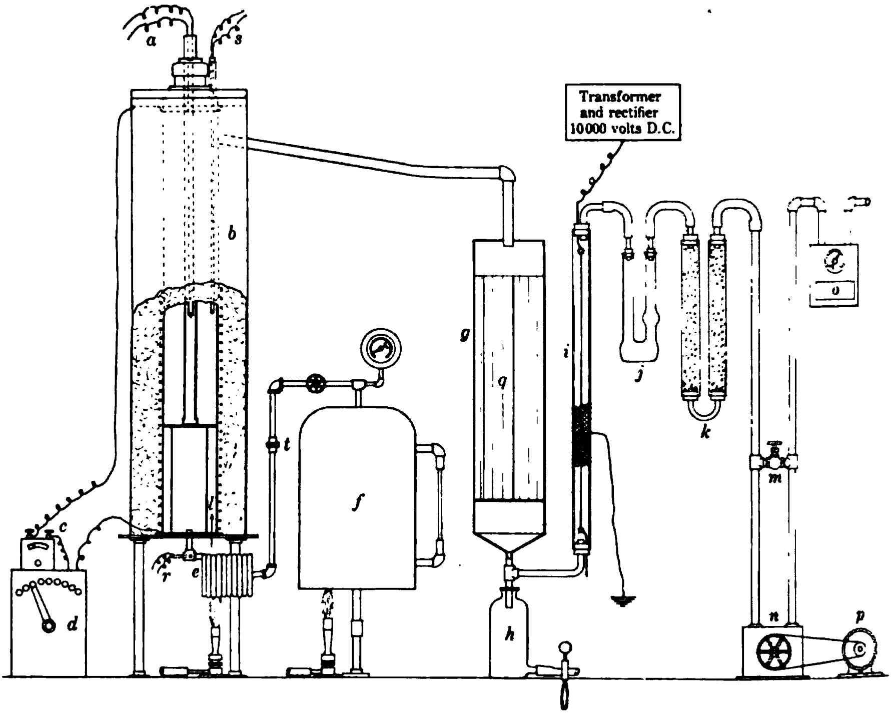

FIGURE 15.—*Apparatus for steam distillation of coal.*

EXPERIMENTAL.

Six kilograms of Freeport coal was used in the experiments. The charge was heated slowly until the temperature of the retort wall registered 300° C.; then the superheated steam was admitted to the retort at a constant rate and temperature for 4 hours, or until coking was complete. A constant supply of steam was obtained by holding the boiler pressure at 20 pounds, and discharging the steam through an orifice measuring 0.05 inch in diameter, which allowed 1.5 liters of water per hour (100 c.c. as water, per pound of coal per hour) to pass into the retort. No trouble was experienced in keeping this steam supply constant. The temperature of the superheated steam was the same as the temperature of distillation, regulation being obtained by a blast burner. Heating of the charge by means of the electric current was continued until the wall thermocouple registered the desired temperature, then the heat input was regulated to keep this temperature constant.

At first, attempts were made to condense the products in two stages by a system of two condensers, one held in steam vapor and the other cooled by tap water, the object being to collect the heavy tars in the hot condenser—avoiding a troublesome emulsion—and to condense the lighter oils and water in a form that would not emulsify. This arrangement was not successful, however, as accurate yields could not be obtained, so the hot condenser was eliminated, and all of the products were condensed together by the water condenser. The remaining by-products were collected in the same number as described on Page 10.

A number of carbonization runs were made at 550°, giving consistent results; then experiments were made with variation of temperature. Table 8 gives a survey of results obtained.

TABLE 8.—*Survey of yields by steam carbonization of Freeport coal.*

Method.	Amount of steam used.	Temperature, °C.	Coke, per cent.	Tar.		Gas, cu. ft. per ton	Ammonium sulphate, per ton
				Per cent.	Gal. per ton.		
Regular carbonization of upper bench Freeport coal without steam....	0	550	70.5	14.0	33	3400	7.0
Carbonizing in same retort in presence of steam....	100 c.c. of water per pound of coal per hour	475	75.0	13.1	30.8	1600	4.5
do.	do.	550	70.8	14.6	33.3	4160	10.0
do.	do.	650	68.0	13.5	50.9	7201	18.3

EFFECT OF STEAM IN CARBONIZATION.

The primary object of the steam is to remove the volatile products from the retort before they would be broken up by coming contact with the hot retort walls. By supplying steam at the rate specified, the retort was swept clean with fresh steam about five times per minute; or, taking into account the volume of the gases formed in the retort, the change was six to seven times per minute, which should materially reduce cracking effects.

At a temperature of 400° a large volume of gas and tar vapors was given off. The efficacy of the electrostatic precipitator was diminished by presence of water vapor, so some of the tar mist passed over into the ammonia scrubber; this trouble, however, lasted only for a short time. Tar and water condensed near the top of the water-cooled condenser, and dripped slowly into the trap; its specific gravity was just a little higher than that of water, which caused an intimate emulsion to form. At intervals, this emulsion was drawn from the trap, and part of the water which floated out was removed by pipetting. After carbonization was complete, the condenser water was heated to remove any tar of higher melting point and a good deal of tar was recovered this way.

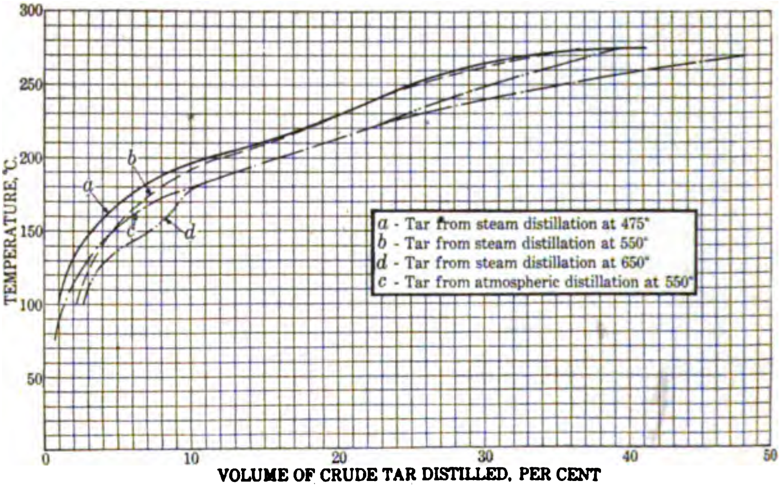

FIGURE 16.—*Distillation of low-temperature tar produced in presence of superheated steam.*

DISCUSSION OF THE PRODUCTS OBTAINED.

TAR.

The emulsion collected in these experiments could only be completely dehydrated by careful distillation at 125° for 10 to

15 hours. The tar recovered was very similar in appearance (color and odor, etc.) to that produced without steam. It was a little more viscous, however, and the Hempel analytical distillation shows it to have marked difference in volatile content. It contains a smaller percentage of light oils but more of the heavier high-boiling fractions. Curves shown in Figures 16 and 17 give the variation in the boiling range of the tar produced at different temperature with and without steam.

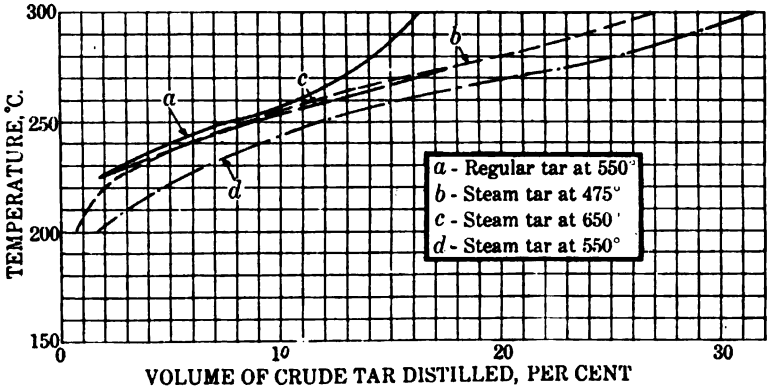

FIGURE 17.—*Vacuum distillation of low-temperature tar at 40 mm. pressure produced by carbonizing in presence of superheated steam.*

Tar produced by distillation with superheated steam is essentially a primary product. One function of the steam is to reduce the partial pressure of the tar vapors, and to sweep them from the retort before decomposition takes place. Also, the steam serves to distribute the heat more uniformly in the retort and to hasten the coking process. For tar obtained by distillation of a gas coal with superheated steam at 500°, Gluud[24] reports a yield of 10 per cent of the charge. Parr and Olin[25] report the amount of tar recovered as representing one-half of the yield of volatile matter, or about 8 per cent of the coal. The writers of this bulletin obtained a yield of approximately 13 per cent at 550°. This yield coincides with that obtained—namely, 13.1 per cent—by Davis and Berger[26] in a previous investigation by distilling coal in vacuo. Table 9 shows the boiling ranges of tar produced by certain investigators.

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[24] Work cited.

[25] Bull. 60. work cited.

[26] Work cited.

TABLE 9.—*Boiling ranges of tars produced by certain investigators.*

Boiling Range, °C.	Yields, Per Cent of Tar.			
	Gluud.	Parr and Olin.	Davis and Parry.	Davis and Berger.
0-100	3.0	10.5	2.3	to 2.7
100-200	10.0	29.1	9.5	4.2
200-300	12.5	35.3	25.0	...
			(in vacuo)	(in vacuo)
300-pitch	15.0	....	31.6	82.0
Pitch or coke residue	....	21.3	31.6	....

It will be noted that there is a variation in the results reported, which is no doubt due to different temperatures of distillation and apparatus employed.

In the Hempel analytical distillation of the steam tar, considerable trouble was experienced in conducting the vacuum distillation. The tar would not distill uniformly under reduced pressure, at a temperature of 200°; there was much bumping and foaming, which indicated the presence of water. On cooling the apparatus, small drops of water formed on the neck of the distillation flask, which may have been formed from the oxygenated compounds in the oil which were broken up at that distillation temperature. This difficulty was overcome by evaporating the water formed and re-distilling. All of the steam tars showed this characteristic, whereas no trouble was experienced at all with distillation of the tar from regular carbonization. The same methods employed in previous work were used in examining the different cuts from the Hempel analysis; the results of which are given in Table 10, following:

TABLE 10.—*Examination of tars from steam distillation.*

	% soluble in 10% NaOH; % of crude cut (tar acids).	% soluble in 95% H_2SO_4, unsaturated material; % of crude cut.	% saturated residue; % of crude cut.	Specific gravity, crude cut.
Produced at 475° C.				
0-175	10.0	37.0	63.0	0.814
175-225	36.0	23.0	41	0.910
225-275	22.5	47.2	30.3	0.951
Produced at 550° C.				
0-175	8.4	38.5	53.1	0.814
175-225	40.0	23.0	37.0	0.920
225-275	26.3	43.4	30.3	0.955
Produced at 650° C.				
0-175	9.0	29.0	62.0	0.823
175-225	36.0	26.0	38.0	0.924
225-275	25.0	43.0	32.0	0.960
Regular tar produced at 550° C.				
0-175	14.5	35.0	50.5	.....
175-225	46.0	25.0	30.0	.....
225-275	30.0	44.0	26.0	.....

Characteristics of the vacuum fractions were not studied thoroughly on account of the lack of time. The cuts to 250° were fluid at room temperature, and when freshly distilled they were of a cherry color; but they gradually changed to a darker shade when exposed to the air. Above the 250° cut the fractions were solid, being of about the consistence of vaseline. The increased quantity of the vacuum fractions, or high-boiling hydrocarbons, from the steam distillation would indicate high recovery of lubricating stock from the tar. Direct comparison of the tars obtained with and without steam is shown in Table 11.

TABLE 11.—*Comparison of tars produced with and without steam.*

Cuts.	Tar produced without steam, %.	Tar produced with steam, %.
Tops 0 to 275° C.	46.0	36.5
Vacuum cut 40-mm. pressure 0 to 300° C.	18.0	31.6
Pitch	40.0	31.9

LIGHT OIL.

The efficiency of the charcoal absorber was materially reduced by the presence of hydrogen sulphide and excess water in the gas; the charcoal took up the H_2S, the water becoming abnormally heated thereby. A low grade of light oil was obtained with charcoal, so a series of four wash-bottles containing straw oil was substituted for this absorbent, and better results were obtained. However, only a small amount of light oil was obtained in carbonizing with steam, one gallon per ton being recovered as compared with three in the regular carbonization without steam.

AMMONIA.

Practically all of the ammonia was taken up by the condensed steam, and the quantity collected was determined by the distillation method previously referred to. By referring to Table 8 we see that the yield of ammonia increased with the temperature, and that carbonization with steam also increases the yield.

GAS.

Table 12 gives the analyses of the various gases obtained in the experiments with and without steam.

TABLE 12.—*Analyses of gases produced with and without steam.*

Gas.	Without Steam.		With Steam.		
	At 550° C.	At 600-650° C.	At 475° C.	At 550° C.	At 650° C.
CO_2	2.2	2.7	3.7	4.1	5.6
C_2H_4	2.3	3.9	4.4	2.0	2.8
O_2	0.8	0.3	2.6	1.4	0.7
H_2	28.1	47.2	12.5	29.1	51.8
CO	4.1	5.5	3.4	4.3	7.2
CH_4	47.1	33.7	38.7	44.2	24.0
C_2H_6	7.8	4.4	18.0	6.7	5.8
N_2	7.6	2.8	16.7	8.2	2.1
H_2S		(No analysis made)			
B. t. u.—Cal.	683.7	681.2	.....	639.6	.....
Cu. ft.	3400	7175	1500	4100	7200

It is interesting to note the variations in the gas analysis, especially variation in the hydrogen and methane content. A steady increase in the former with increase of temperature will be noted. These same variations were established by Lewes[27], Burgess and Wheeler[28], and Porter and Ovitz[29]. According to Porter and Taylor[30] the sudden liberation of hydrogen is due to secondary decomposition of the tars. It will be noted from the analysis that hydrogen is evolved more rapidly above 550°. According to Lewes—

> Methane, which is next in importance to hydrogen in the high-temperature gas, is a product of both primary and secondary reactions; and being the most stable of the gaseous hydrocarbons, undergoes destruction only at high temperatures, so that for the methane to fall below 30 per cent in a coal gas made from a good gas coal means degradation of the products by overheating.

It will be noted that the percentage of methane decreases sharply between 550 and 650° and that it has maximum percentage at 550°. This would go to show that between 500 and 550° is a critical temperature for secondary decomposition products. Higher percentage of saturated hydrocarbons is obtained in the gas at distillation temperature of 475°. The ethane is evidently a primary decomposition product of the coal, and is sensitive to temperatures around 500°, breaking down into hydrogen and methane.

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[27] Work cited.

[28] Burgess, M. J., and Wheeler, R. V., Volatile constituents of coal: *Jour.* Chem. Soc., vol. 99, 1911, p. 649.

[29] Porter, H. C., and Ovitz, F. K., The volatile matter of coal: Bull. 1, Bureau of Mines, 1910, 56 pp.

[30] Porter, H. C., and Taylor, G. B., The primary volatile products of the carbonization of coal: a sequel to Bull. 1: Tech. Paper 140, Bureau of Mines, 1916, 59 pp.

COKE.

The coke obtained in the experiments with steam showed considerable variation with the different temperatures of retorting.

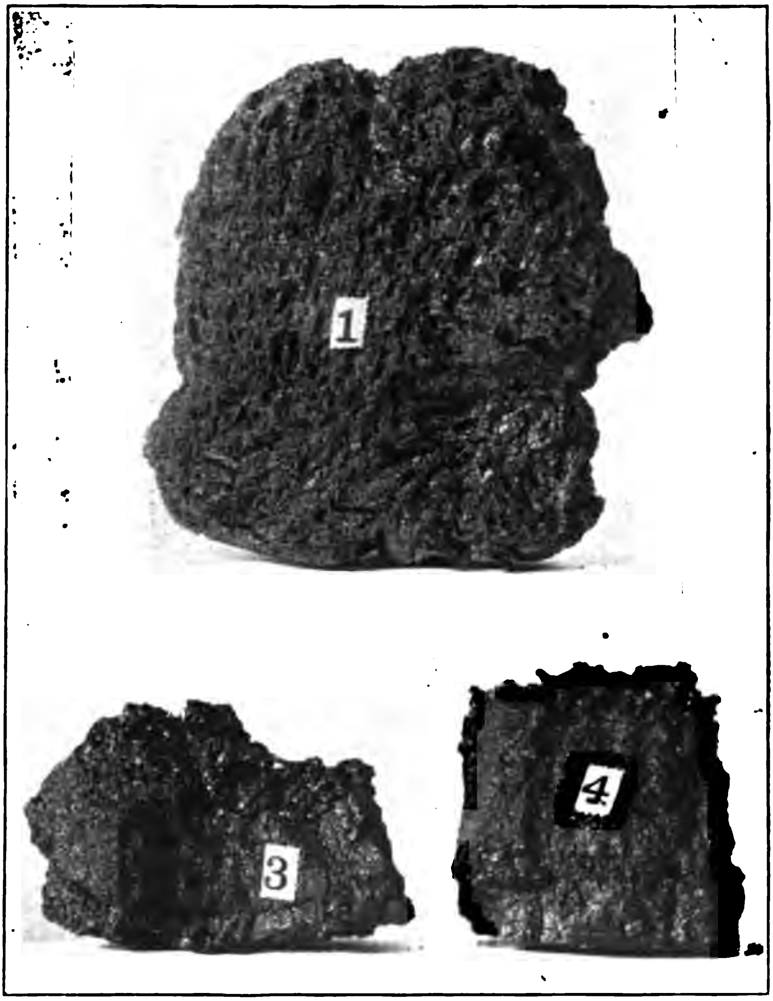

FIGURE 18.—*Coke obtained by carbonizing Freeport coal with steam— No. 1 at 475° C., No. 3 at 550° C., and No. 4 at 650° C.*

Table 13 gives the analysis while Figure 18 shows typical cokes obtained. The comparative yields were as follows:

No.	Coke carbonized at, °C.	Per cent.
1	475[a]	74.3
2	550[b]	70.7
3	550[a]	70.8
4	650[b]	68.0

[a] *With steam.*
[b] *Without steam.*

The coke from distillation at 475° was black and spongy, and contained large bubbles of partly carbonized tar; also a concentric ring of irregular formation filled with large blowholes and covered with shiny pitch, ¾ inch from the wall. Farther in, for a space of 1½ inches, the structure was more regular with smaller holes, but of the same black shiny appearance. At the center of the mass was a small opening where some of the tar vapors escaped from the coal, and around this the structure was irregular. The coke had swelled considerably, but was not difficult to remove from the retort; it broke up easily into fines. The carbonized product from the distillation at 550° was of much denser structure than the preceding coke, there being several concentric rings of different structure, and next to the wall the coke was porous but of greyish color, showing more complete carbonization. The action of the steam evidently was responsible for this porous layer. Farther in, the coke exhibited a denser structure, similar to that obtained in carbonizing without steam, so evidently the steam had not penetrated well into this region. A larger hole appeared at the center of the mass, and around this the structure was again porous and somewhat black and shiny, similar to the coke produced at 475°. It is evident that there was not uniform distribution of the steam through the charge, which could only be ensured by agitation during carbonization. The coke obtained in the distillation at 650° was very similar in appearance to that at 550°, but slightly more grey.

Referring to the analysis, it is interesting to note the change of volatile content of the coke. Most of the investigators in low-temperature carbonization have reported yields of coke of 70 to 75 per cent of the coal, and containing approximately 10 per cent of volatile matter. The coke obtained by the writers at 550° falls within these figures, which indicates that 500 to 550° is a good temperature for low-temperature coking of this particular coal.

TABLE 13.—*Analyses of coke from carbonization with steam.*

Method.	Proximate Analysis.				Ultimate Analysis.					Calorific value, B. t. u.
	Moisture.	Volatile matter.	Fixed carbon.	Ash.	Hydrogen.	Carbon.	Nitrogen.	Oxygen.	Sulphur.	
Original coal............................	(a) 1.5	39.3	54.7	4.6	3.5	78.9	1.7	7.5	1.8	14240
	(b) ...	39.8	55.5	4.7	5.4	80.1	1.7	6.3	1.8	14450
	(c) ...	41.7	58.3	...	5.7	84.0	1.8	6.6	1.9	15150
Carbonized with steam at 475° C............	(a) 0.3	16.5	76.9	6.3	3.8	81.4	2.0	4.7	1.0	13900
	(b) ...	16.6	77.1	6.3	3.8	81.6	2.0	4.5	1.8	13940
	(c) ...	17.7	82.3	...	4.0	87.1	2.1	4.8	2.0	14880
Carbonized with steam at 550° C............	(a) 0.9	8.4	84.2	6.5	2.7	83.9	2.1	3.7	1.1	13820
	(b) ...	8.5	84.9	6.6	2.7	84.7	2.1	2.8	1.1	13950
	(c) ...	9.1	90.9	...	2.8	90.6	2.2	3.2	1.2	14920
Carbonized with steam at 650° C............	(a) 1.3	7.9	83.9	6.9	2.5	83.9	2.0	3.7	1.0	13610
	(b) ...	8.0	85.0	7.0	2.4	85.0	2.0	2.6	1.0	13790
	(c) ...	8.6	91.4	...	2.6	91.3	2.2	2.8	1.1	14820
Carbonized without steam at 550° C.........	(a) 0.7	8.5	83.4	7.4	2.9	83.0	1.9	3.0	1.8	13720
	(c) ...	9.3	90.7	...	3.0	90.3	2.0	2.7	2.0	14930

[a] *As received.*
[b] *Moisture free.*
[c] *Moisture and ash free.*

INVESTIGATION OF LOW-TEMPERATURE TAR WITH SPECIAL REFERENCE TO THE RECOVERY OF LIGHT OILS OF VALUE AS MOTOR FUEL.

Despite all of the chemical investigation that has been carried on by numerous investigators, the industrial utilization of low-temperature tar is still a problem. Probably its chief value at the present time lies in its use as a fuel oil for metallurgical furnaces or for raising steam. One marketable product that can be recovered from low-temperature tar is motor fuel.

Previous investigators have reported yields of this product varying from 0.64 to 17.2 per cent of the crude tar. Comparison of the yields is difficult because of the wide difference in conditions of retorting and in analytical methods for evaluating the tar. However, comparative figures of yields of light oil, as determined by several investigators, are as given in Table 14.

In the present investigation of low-temperature carbonization of Pennsylvania coals, the writers paid special attention to the maximum yield of products of value as motor fuel. Although the methods of carbonizing at low temperatures differ widely, and the tar varies accordingly, the following figures and experiments give an index of the amount of light oil that can be recovered from a Pennsylvania bituminous coal by carbonizing at 550° in a stationary vertical retort. The yields of light-oil in this investigation were determined from:

1. The amount absorbed from the gas by activated charcoal.
2. The fraction of the tar boiling under 175° C. in the Hempel analytical distillation.
3. The amount recoverable by cracking in vapor phase the neutral oil fraction 175° to 275° C.
4. The amount recoverable by reduction of the tar acids; but time did not permit of completion of these experiments.

SOURCE OF TAR.

In order to obtain a sufficient quantity of tar for examination, a number of runs were made on Freeport coal at 550°. In all of these tests the carbonization was carried on in the same manner as shown in Figure 14. Six kilograms of low-temperature tar was thus obtained, and this was fractionated in a large cast-iron retort

TABLE 14.—*Comparison of yields of light oils obtained by certain investigators.*

Investigator.	Type of Coal.	Method of carbonization.	Maximum carbonization temperature, °C.	Yield of light oil, per cent of tar.	Maximum temperature of cut, °C.
Lewes[a]	Gas coal		400-500	8.10	170
Parr[b]	Illinois coal	External and internal	750-800	17.2	210
Gluud[c]		Internal	500	13.0	200
Runge[d]	By-product	Continuous, external heating	730	3 gallons per ton on 24 to 30 gallons total tar	10-12.5%
Davis and Berger[e]	Freeport by-product	External heating	600-650	6.8	175
Morgan and Soule[f]	Pittsburgh Terminal	Continuous, external heating	730	0.64	173
Davis and Parry	Freeport	External heating	550	8.5 in tar 7.0 in gas	175

[a] Lewes, V. B., Carbonization of coal, 1912, p. 192.

[b] Parr, S. W., and Olin, H. L., Coking of coal at low temperatures with special reference to the properties and composition of the product: Univ. of Illinois Eng. Exp. Sta. Bull. 99, 1915, p. 22.

[c] Work cited.

[d] Runge, Walter, Products of low temperature distillation of coal: *Chem. Age*, vol. 30, No. 1, 1922, p. 9.

[e] Work cited.

[f] Morgan, J. J., and Soule, R. P., Studies in the carbonization of coal; characteristics of low-temperature coal tar: *Chem. and Met. Eng.*, vol. 26, 1922, p. 23.

with a Hempel fractionating column as shown in Figure 19. This still was designed to maintain conditions similar to the small-scale

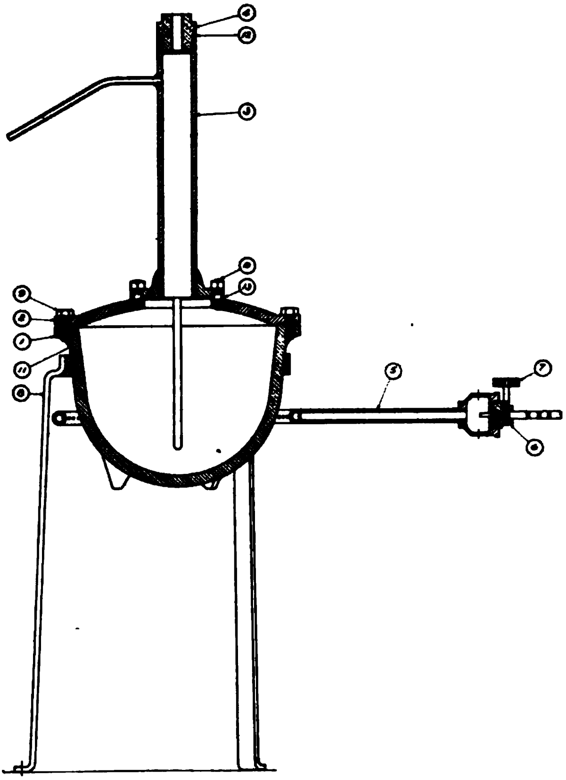

FIGURE 19.—*Large-scale Hempel apparatus.*

Hempel analytical distillation. Following are the cuts collected:

	% of crude tar.	Specific gravity.
Light oil, 0-175°	8.5	0.853
Middle oil, 175-225°	16.0	0.962
Heavy oil, 225-275°	19.5	0 998
280-350° anthracene	11.2	Not determined
	55.2	

The total distillate under 200° C. was 13.0 per cent.

The fraction boiling under 175° was considered crude light-oil stock; it contained 17 per cent of tar acids and 42 per cent of unsaturated hydrocarbons. The fractions boiling between 175 and 275° were treated with caustic to remove the tar acids, and the remaining oil was the basis for the following cracking experiments.

APPARATUS FOR CRACKING IN VAPOR PHASE.

Figure 20 shows the apparatus[31] used in the cracking experiments on neutral oil from low temperature tar, in complete detail.

EXPERIMENTAL.

Four hundred cubic centimeters of oil of 0.904 specific gravity was placed in the reservoir and fed into the preheater, which was held at constant temperature of 400° C., at the rate of 30 drops per minute. The vaporized oil then passed into the cracking chamber, where it was subjected to the desired cracking temperature. Temperature measurements were made by a thermocouple placed in the center of the furnace at the wall of the cracking tube, and the regulation was close. When the apparatus was running smoothly, gas samples were taken, the system being held at atmospheric pressure meanwhile. Table 15 gives the results, while Figure 21 is a diagrammatic representation of the yields.

TABLE 15.—*Survey of yields from cracking experiments on neutral oil, 175 to 275 C.*

Cracking, temperature, °C.	Oil recovered.	Specific gravity at 15.5° C.	Per cent recovered.	Per cent original crude tar.	Gas.		Light oil in scrubber, c.c.	Per Cent.
					Cubic feet.	Cu. ft. per gal.		
650	365	0.908	91.2	20.6	0.6	5.7	1.8	0.5
750	253	0.972	63.0	14.2	2.81	26.6	7.0	1.8
820	193	1.060	48.3	10.9	5.2	49.2	20.0	5.0
	Anthracene neutral oil, 275° to 350° C., 400 c.c. treated							
800	199	1.114	49.8	4.3	5.0	47.2	9.0	2.2

In 1916, Egloff and Twomey[32] studied the effects of temperature on gas oil in the vapor phase, and the results obtained in the present investigation fall along comparatively the same lines as recorded by them. It was noted in the distillation analysis of the recovered light oil from the scrubber that it contained a large percentage of hydrocarbons boiling at about 80° C., indicating the

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[21] This apparatus is the one used by J. J. Jakosky of the Pittsburgh Experiment Station in his experiments on cracking petroleum gas oil in the vapor phase using the corona discharge. His results are to be published in a paper entitled "Effect of high-frequency discharges on the cracking of petroleum".

[32] Egloff, Gustav, and Twomey, Thomas J., Effect of temperature on the formation of benzene, etc. (and higher hydrocarbons): *Jour. of Physical Chem.*, vol. 20, 1916, pp. 121-150.

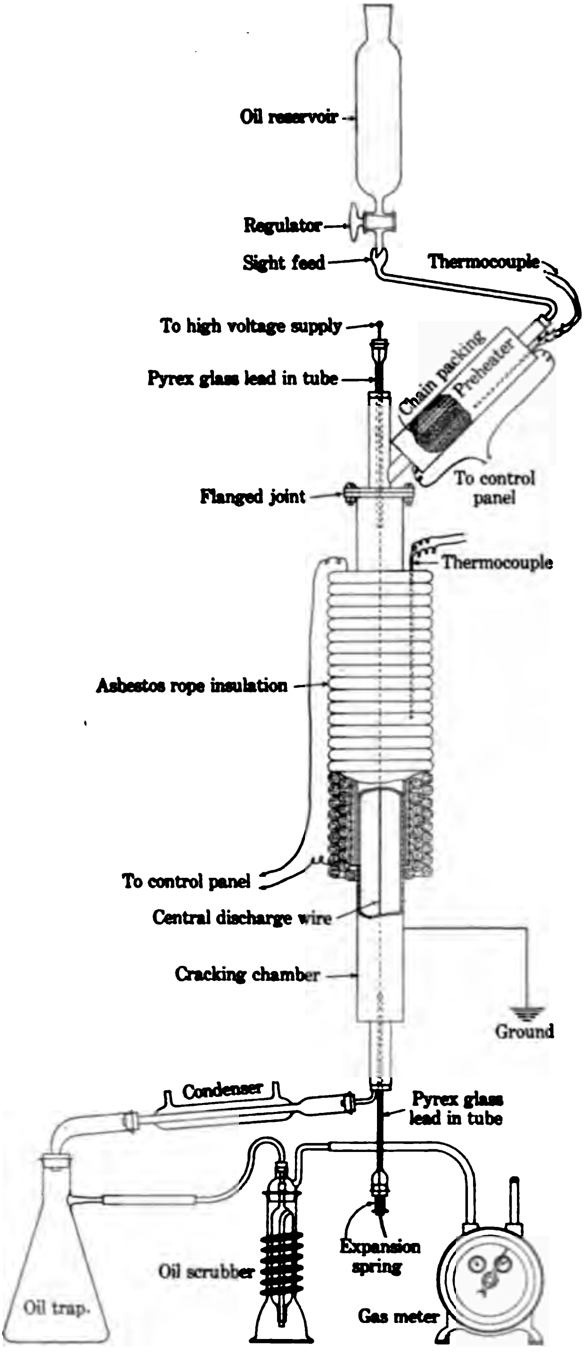

FIGURE 20.—*Apparatus used in studying effect of corona discharge during cracking.*

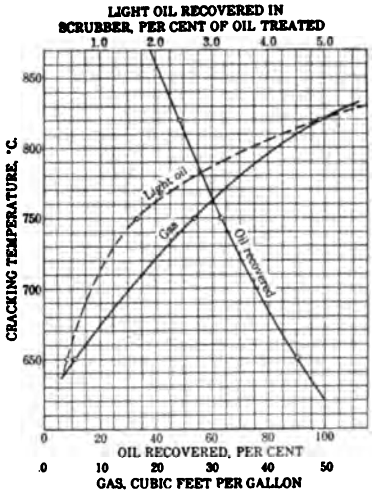

FIGURE 21.—*Curves showing effect of temperature in cracking neutral oils of the fraction (175° to 275° C.) from low-temperature carbonization of Freeport coal.*

presence of benzene. The following tables (16, 17, and 18) give the Hempel analysis of the neutral oil, before and after the cracking experiments:

TABLE 16.—*Hempel analysis of cracked oils.*

Oil.	Temperature, °C.	Volume distilled, c.c.	Per cent sum.	Per cent of original neutral oil.	Per cent of crude tar.	Unsaturation.	Specific gravity.
Original neutral oil....	100	1.5	0.5	0.5	....	..	.....
	125	4.0	1.3	1.3	0.3	..	.....
	150	11.0	3.7	3.7	0.8	..	.....
	175	27.0	9.0	9.0	2.0	..	.....
	200	60.0	20.0	20.0	4.5	..	.....
	225	112.0	37.0	37.0	8.3	..	.....
	250	173.0	58.0	58.0	13.0	..	.....
Oil cracked at 650° C. (91.2% recovered)...	50	2.0	0.7	0.6	....		
	75	6.0	2.0	1.8	0.4		
	100	8.0	2.7	2.5	0.6	59	0.816
	125	15.0	5.0	4.5	1.0		
	150	23.0	7.7	7.0	1.6		
	175	42.0	14.0	12.7	2.9		
	200	80.0	26.6	24.2	5.5	60	0.802
	225	127.0	42.3	38.5	6.7		
	235	150	50.0	45.6	10.3	61	0.914
Oil cracked at 750° C. (63.0% recovered)...	50	1.0	0.5	0.3	....		
	75	3.0	1.5	1.0	0.2		
	100	9.0	4.5	2.8	0.6	68	0.854
	125	17.0	8.5	5.3	1.2		
	150	27.0	13.5	8.5	1.9		
	175	43.0	21.5	13.5	3.1		
	200	63.0	31.5	19.8	4.5	70	0.930
	225	87.0	43.5	27.3	6.2		
	237	103.0	51.5	32.5	7.3	72	0.964
Oil cracked at 820° C. (48.3% recovered)...	75	5.0	3.2	1.5	0.3		
	100	12.0	7.7	3.7	0.8		
	125	13.5	8.6	4.1	0.9	70	0.887
	150	20.6	13.1	6.3	1.4		
	175	27.2	17.3	8.3	1.9		
	200	35.0	22.3	10.7	2.4	..	0.978
	225	54.0	34.4	16.5	3.8		
	250	80.0	50.8	25.0	5.6	..	1.010

TABLE 17.—*Hempel analysis of neutral anthracene oil, 275 to 350° C.*

(This oil represents 8.6 per cent of original crude tar. Volume distilled, 300 c.c.; specific gravity, 0.998; first drop, 100°.)

Temperature, °C.	Volume distilled, c.c.	Per cent sum.	Per cent of original crude tar.
160	10.0	3.0	0.3
175	13.0	4.3	0.35
210	23.0	7.7	0.65
250	34.0	11.3	0.97

TABLE 18.—*Hempel distillation of neutral anthracene oil after cracking at 800° C.*

(Volume distilled, 199 c.c.; first drop, 57°; recovered, 50 per cent; specific gravity, 1.114.)

Temperature, °C.	Volume distilled, c.c.	Per cent sum.	Per cent of original neutral oil.	Per cent of crude tar.	Specific gravity.
75	5.0	2.5	1.2	0.1	0.877
100	8.5	4.3	2.1	0.2	
125	10.5	5.3	2.6	0.24	
150	14.0	7.0	3.5	0.3	
175	17.0	8.5	4.3	0.37	
200	23.0	11.5	5.3	0.5	70% solid $C_{10}H_8$
225	34.0	17.0	8.5	0.7	......
250	50.0	25.0	12.5	1.1	1.027

In his experiments on the cracking of gas oil using high-frequency current and the same apparatus, Jakosky[**] did work that was comparable to the foregoing experiments on the neutral oil from low-temperature tar. His work covered the same temperature, with and without the high-frequency current, and Tables 19 and 20 give some of his results without the high-frequency discharge.

COMPARISON OF THE EFFECTS OF TEMPERATURE ON NEUTRAL TAR OIL AND PETROLEUM GAS OIL.

From the foregoing experiments some conclusions may be drawn as to the comparative value of low-temperature oil and gas oil. Evidently the optimum cracking temperature for the greatest yield of light fraction from tar oil is 750°, while 800° is the optimum temperature for gas oil. Much more hydrogen is liberated from the tar oil, which would indicate high unsaturation in the liquid recovered, which is shown to be the case. Not much difference exists in the heating value of the gas, but a greater yield is obtained from the gas oil. In regard to the amount of oil re-

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[**] Personal communication, June, 1923. See also reference 31.

TABLE 19.—*Hempel analysis of gas oil.*

Oil.	Temperature, °C.	Sum per cent distilled.	Per cent of original oil.	Per cent recovered.	Gas recovered, cu. ft. per gal.
Original gas oil.	75	.....	.....	....	..
	100	.....	.....	....	..
	125	.....	.....	....	..
	150	.....	.....	....	..
	175	.....	.....	....	..
	200	2.5	.....	....	..
	250	18.7	.....	....	..
	275	33.0	.....	....	..
Oil cracked at 600° C.	75	0.33	0.32	96.2	12
	100	1.16	1.12	....	..
	125	1.66	1.60	....	..
	150	2.49	2.40	....	..
	175	3.92	3.75	....	..
	200	6.52	6.27	....	..
	225	13.0	12.5	....	..
	250	24.6	23.6	....	..
	275	39.6	38.0	....	..
Oil cracked at 700° C.	75	5.6	3.7	75.0	33
	100	6.0	4.5	....	..
	125	.....	....	....	..
	150	12.34	9.2	....	..
	175	14.67	11.0	....	..
	200	18.34	13.7	....	..
	225	23.34	17.5	....	..
	250	34.34	23.7	....	..
	275	43.34	36.3	....	..
Oil cracked at 800° C.	75	2.6	1.6	63.2	43
	100	7.11	4.5	....	..
	125	.....	.....	....	..
	150	.....	.....	....	..
	175	22.21	14.0	....	..
	200	28.88	18.2	....	..
	225	35.55	22.4	....	..
	250	48.77	28.8	....	..
	275	58.65	37.0	....	..

TABLE 20.—*Analysis of gases obtained in cracking experiments.*

Gas.	Neutral oil 175-275°.			Anthracene oil.	Gas oil.		
	Cracking temperature.			Cracking temperature.	Cracking temperature.		
	650°	750°	820°	800°	600°	700°	800°
CO_2	0.3	0.2	0.0	0.2	1.3	0.2	0.0
C_2H_4	38.9	36.2	21.6	18.0	22.0	50.0	33.3
O_2	0.5	2.8	0.2	0.2	7.1	1.1	5.3
H_2	6.1	5.4	17.4	20.7	1.5	4.6	5.1
CO	0.8	0.5	2.1	4.6	0.9	0.6	0.5
CH_4	36.1	33.9	56.1	53.5	11.2	25.3	28.8
C_2H_6	15.1	10.3	2.0	1.6	12.2	15.2	8.7
N_2	2.2	10.7	0.6	1.2	43.3	3.0	18.3
B. t. u.	1175	1035	940	856	538	1241.8	922.1
Yield, cu. ft. per gal.	9.0	33.0	50.0	....	12.0	34.0	63.0

covered at each temperature, both oils exhibit practically the same tendencies; also the fraction boiling under 175° C. is about the same. So we can see that the neutral, middle, and heavy-oil fractions from low-temperature tar are comparable with the gas-oil fraction from petroleum.

TAR ACIDS AS A SOURCE OF LIGHT OIL.

The tar acids or phenolic compounds of low-temperature tar are another possible source of motor-spirit stock. This possibility has been shown recently by the experiements of Fischer and Schraeder[24] in Germany, according to whom—

> Low-temperature tar consists of hydrocarbons similar to those of petroleum, and of phenols, but no aromatic hydrocarbons. The benzene homologues in coal tar must be formed from phenols, since the other group can only be converted into aromatics to the extent of a few per cent. In support of this view the authors report the result of passing mixtures of H_2 with phenols and hydrocarbons through tubes heated to 750°. Separation of the free carbon was found to depend largely on the nature of the wall, being negligible in a porcelain tube and very considerable in an iron tube; tinned iron was found to be a technically practical material which did not cause separation of carbon. Under these conditions the phenols were reduced to benzene homologues. Seventy-two per cent conversion was obtained with the cresols and xylenols, while the hexane present was very little affected.

Acting upon this indication of motor-fuel possibilities from the phenols, the writers attempted to obtain some data upon the reduction of the phenols extracted from the tar collected in the present investigation. Figure 22 is a detailed diagram of the apparatus used in the experimental work.

EXPERIMENTAL.

One hundred cubic centimeters of the tar acids were placed in the vaporizer and distilled slowly by means of a Bunsen burner, so that the vapors were passed into the reduction chamber at a rate of 0.5 c.c. per minute. An excess of hydrogen was intermixed with the vapors in the vaporizer. Any reduction products or unreduced material was collected by the condenser or the charcoal absorber, and the fixed gases were measured by the gas meter.

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[24] Fischer, Franz, Uber die Herstellung leichter Motorinbetriebstoffe aus den Urteer de Steinkohle und der Braunkohle, inbesondere uver die Verandlung der Phenols beziehungsweese des Kreosote in Benzol: *Brennstoff-Chemie*, Nov. 15, 1921, heft 22.

Fischer, Franz, and Schraeder, Hans, What is the source of benzene in coke ovens and gas retorts? *Brennstoff Chemie* 1, 1920, pp. 4-6.

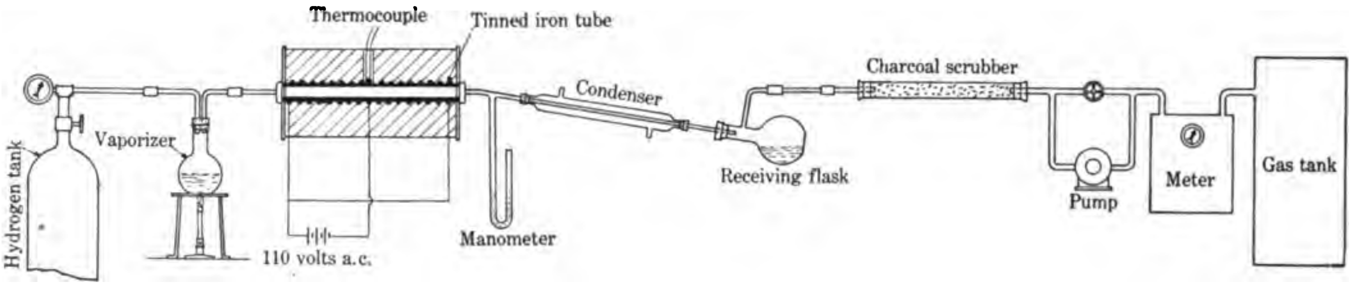

FIGURE 22.—*Apparatus for reduction of tar acids.*

RESULTS FROM REDUCTION TEST ON PHENOLS FROM TAR.

Much gas was formed, but in the condensed liquor there was no evidence of any reduction. Time did not permit of any extended work on this material, so further experimental work was abandoned. However, this problem offers interesting possibilities, and there is no doubt that the value of low-temperature tar would be materially increased by its successful solution on an industrial basis.

Fischer[85] obtained a reduction of 72 per cent of these tar acids into benzene and benzene homologues. In carbonizing one ton of Freeport coal at 550° C., 5.5 gallons of these compounds would be obtained, and by reduction of 72 per cent, approximately 4 gallons of motor spirit would result. This comparatively high yield is nearly equivalent to the total amount derived from the remainder of the tar.

SUMMARY OF YIELD OF LIGHT OIL FROM LOW-TEMPERATURE TAR.

I. Crude tar. — 33 gallons per ton = 14.6 per cent of coal.
  A. Light-oil cut 0 to 175° C. = 9 per cent = 3 gallons per ton.
    1. Refining loss = 1.15 gallons per ton, including tar acids.
      (a) Tar acids = 14.5 per cent = 0.45 gallon per ton = 0.16 per cent of coal.
      (b) Unsaturated material = 23 per cent = 0.70 gallon.
    2. Refined light oil from straight distillation = 3.0 — 1.15 = 1.85 gallons.
  B. Middle and heavy-oil cut 175° to 275° C. = 38.0 per cent = 12.5 gallons per ton.
    1. Refining loss of tar acids = 40.0 per cent = 5.0 gallons per ton.
    2. Neutral oil (including unsaturated material) = 60 per cent = 7.5 gallons = 22.6 per cent of crude tar.
      (a) Cracking at 750° C. atmospheric pressure.
        1. Light-oil boiling under 175° in recovered oil = 13.6 per cent of original oil = 3.1 per cent of crude tar = 1.05 gallons per ton. Refining loss of this fraction is 56 per cent. Net light oil from recovered oil = 0.46 gallon.
        2. Light-oil from scrubbing gases of cracked oil = 2 per cent = 0.15 gallon per ton. Refining loss = 28 per cent = 0.04 gallon. Net refined light-oil from gas = 0.11 gallon.
    3. Total refined light oil from cracking = 0.57 gallon.
  C. Light oil scrubbed from gases during carbonization, by activated charcoal.
    1. Yield = 2.9 gallons per ton of coal carbonized; 35 per cent unsaturated.
      (a) Refining loss = 23 per cent = 0.66 gallon.
      (b) Net refined light oil from gas = 2.24 gallons.
  D. Net crude light oil from one ton of Freeport coal = 7.10 gallons.
  E. Net refined light oil from one ton of Freeport coal = 4.66 gallons. Refining loss = 34.5 per cent.

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[85] Work cited.

The crude light oil obtained from high-temperature treatment is 2 to 3 gallons per ton of coal carbonized, and comparing this yield with that obtainable from low-temperature treatment, it will be seen that there is only a comparatively small increase. However, by increasing the light-oil fraction to include distillates below 200°, the refined motor-fuel stock would reach about 5.8 gallons per ton of coal carbonized, which amount would place light oil as one of the major by-products.

CONCLUSIONS.

From the data obtained in this investigation the following conclusions can be drawn:

1. The regular Pittsburgh bed coal is a good low-temperature coking coal. When carbonized at 550° C. in a stationary vertical retort it will yield 33 to 35 gallons of tar, 3500 cubic feet of 600 B.t.u. gas, 1400 pounds of 10 per cent volatile coke, and 6 to 8 pounds of ammonium sulphate per ton.

2. The other parts of the Pittsburgh bed—namely, the rooster, the lower roof, and the upper roof—are of similar coking quality, differing only in the quantity of by-products yielded. These decrease in the order given. The yield of tar from the upper roof is only 66 per cent that from the regular seam, and from the rooster coal 75 per cent. The difference is largely due to the variation in the ash content of the different sections, and not to the chemical composition of the coals.

3. Microscopic study of the various parts of the Pittsburgh bed by Thiessen and Straud[36] shows them to have similar structure and a preponderance of spore matter throughout. This indicates the same conditions of formation, and accounts for the similarity in quality of the yields on coking.

4. In comparing the Pittsburgh, Freeport, and Upper Kittanning coals under similar methods of carbonizing, we find that the Pittsburgh and Freeport coals are similar in the amount and quality of the by-products. However, the bony sections of the Freeport bed, as determined by Davis and Berger[37] show smaller value than the bony roof coals of the Pittsburgh bed, the bone and cannel coals of the Freeport bed being not nearly so good as the bony coals of the Pittsburgh bed; the difference is mainly due to the higher ash content of the Freeport bony coals.

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[36] Thiessen, Reinhardt, and Staud, J. N., Correlation of the coal beds in the Monongahela formation in Ohio, Pennsylvania, and West Virginia: Bull. 9, Carnegie Inst. of Tech., 1923, 64 pp.

[37] Work cited.

The Upper Kittanning coal is not a good low-temperature coking coal. The coke is not dense, and the yield of by-products is low. This is a semi-bituminous coal with low volatile matter, and was not expected to yield much tar.

5. For rational analysis of the tars, the standard Hempel method for atmospheric and vacuum distillation gave consistent results; and it is the opinion of the writers that it should be adopted as a standard for the examination of low-temperature tars.

6. The characteristics of the tars from the different coals tested were very similar, as shown by the Hempel analysis and by treatment with acid and caustic—namely, 8.5 to 9.0 per cent distilled under 175° C., 18.0 to 20.0 per cent between 175 and 225° C., and 20 to 22 per cent above 225° C.

7. The total amount of crude light oil suitable for motor fuel that was obtained directly from Pittsburgh or Freeport coal by distillation at 550° C., and by cracking is approximately 7.1 gallons per ton, or 2.6 per cent by weight of the coal. The net refined motor fuel from the process is 4.6 gallons per ton, or 1.7 per cent by weight of the coal.

8. Superheated steam has an effect upon the by-products of low-temperature carbonization. The tars obtained were more viscous, and contained a smaller amount of light oils and a larger amount of heavy oils. The amount of the by-products obtained by carbonizing with superheated steam was practically the same as without steam. The steam prevented secondary decomposition to some extent.

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Bulletin 9

COAL-MINING INVESTIGATIONS

UNDER AUSPICES OF

CARNEGIE INSTITUTE OF TECHNOLOGY,
U. S. BUREAU OF MINES, AND
ADVISORY BOARD OF COAL-MINE OPERATORS AND ENGINEERS.

CORRELATION OF COAL BEDS IN THE MONONGAHELA FORMATION OF OHIO, PENNSYLVANIA, AND WEST VIRGINIA.

By
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Bureau of Mines;
and
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Carnegie Institute of Technology.

CARNEGIE INSTITUTE OF TECHNOLOGY,
PITTSBURGH, PENNSYLVANIA.
1923.

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PREFACE.

Pittsburgh is the greatest industrial center in America, and the heart of the greatest bituminous coal-mining district in the world. It is eminently desirable, therefore, that this city should have an institution which devotes a part of its great facilities to the scientific study of that branch of the industry which is largely responsible for Pittsburgh's development and that of western Pennsylvania.

On May 27, 1919, a number of leading representatives of the coal-mining industry of western Pennsylvania met in conference with the President of Carnegie Institute of Technology with a view of bringing about closer relations between the Institute and the mining interests. It was felt that the advice and co-operation of men in the field were necessary for the training of young men for mining work, and at the conclusion of the meeting the following resolution was adopted:

> That this gathering give its approval and moral and material support to the form of education proposed for the Carnegie Institute of Technology by which students may receive a combined technical, practical, and business training, necessary to fit them for service in the coal mining and allied industries. Further, that the President of the Carnegie Institute of Technology appoint a board of no less than ten men representing the coal mining and allied industries, the United States Bureau of Mines, the State Department of Mines, and the Carnegie Institute of Technology, who will advise and assist in carrying out this program of education and training, particularly in its practical phases to the mining industry and in its co-operation with the United States Bureau of Mines.

Following further the intention of this resolution, the President of the Institute entered into a co-operative agreement on June 1, 1919, with the Director of the U. S. Bureau of Mines whereby full advantage could be taken of the Bureau's laboratories, equipment, and library, as well as of the advice and instruction of its technical staff.

To carry out this new program there was organized during the summer months the Co-operative Mining Courses in the Department of Mining and Metallurgical Engineering, College of Engineering, of the Institute. The course in mining engineering covers four years, and leads to the degree of Bachelor of Science. The two-year course in coal mining is planned to prepare men

with a certain amount of practical experience for executive positions. The four-weeks intensive summer course in coal mining is designed for miners who aspire to be firebosses and mine foremen.

In a large measure, the new mining, ore-dressing, and coal-washing laboratories at the Institute have been equipped gratuitously by various manufacturers of mining machinery and appliances. Co-operative research through teaching and research fellowships is devoted to various problems in coal mining and the utilization of fuels. The Institute selects the fellows, the Bureau of Mines provides the laboratory facilities, and the Advisory Board determines what problems be undertaken, and publishes the reports.

The primary object of this co-operation of the Carnegie Institute of Technology, the U. S. Bureau of Mines, and the Advisory Board of Coal Mine Operators and Engineers is the proper education and training of young men for the mining industry. The ultimate objective is to bring about better conditions and greater efficiency in mining operations. The decrease in reserves of coal and increasing cost of production make it urgently necessary for mine operators and engineers to take advantage of everything which modern science, machinery, and methods can contribute.

EDWARD STEIDLE,
Supervisor, Co-operative Mining Courses,
Carnegie Institute of Technology.

FOREWORD.

The investigation described in this paper was conducted by the Co-operative Mining Courses, Department of Mining, Carnegie Institute of Technology, and the Pittsburgh Experiment Station of the Bureau of Mines, in co-operation with the coal-mining industry of western Pennsylvania. Under co-operative agreement, four research fellowships paying $750 per annum per year of ten months are supported by the Carnegie Institute of Technology. These fellowships are open to properly qualified graduates of universities and technical schools. The research work is carried on in the laboratories of the Bureau of Mines, under the direction of a member of the Bureau research staff and is published under the joint authorship of the two investigators.

Fellowship holders are required to register at the Institute as graduate students, and become candidates for the degree of Master of Science, unless an equivalent degree has been previously earned. The purpose of these fellowships is the solution of problems in mining and the utilization of coal.

This bulletin is the second one of a series covering the microscopic study of the coal beds of western Pennsylvania, Ohio, and West Virginia, and includes the three important coal beds of the Monongahela formation—namely, the Sewickley, Redstone, and Pittsburgh beds. The Pittsburgh bed was sampled in four mines in Pennsylvania, two in West Virginia, and one in Ohio; the Redstone bed in two mines in Pennsylvania and one in Ohio; and the Sewickley in three mines in Ohio, one in Pennsylvania and one in West Virginia. A sufficient number of samples were examined to furnish means of identifying these three beds by their characteristic spores and plant structures. The Pittsburgh bed spore is especially characteristic, and serves to identify this bed from the microscopic examination of a single small piece of coal.

Differentiation between the Redstone and Sewickley requires more care, and necessitates the examination of a number of samples from each bed.

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ERRATA

Owing to part of an old list of titles for illustrations becoming mixed with that for the plates in this bulletin, the following corrections should be noted:

Plate IV—Add (See page 16.) The magnification of *A* and *B* is 20; *C*, 200, and *D*, 1000 diameters.

Plate XII A—Substitute "Horizontal" for "Thin cross—"

Plate XIII A—Substitute "Vertical" for "Horizontal".

Plate XIX—Add, *B* and *C* represent the same spore shown in Plate XX, more highly magnified. *D* shows this spore doubled upon itself, a fairly common occurrence. The granular nature is particularly well shown, X 1000".

Plate XX—After word "spores", line 2, substitute "shown at a higher magnification in Plates XXI *A* and *B*, and XXII *C*. X 200."

Plate XXII—Omit word "than", line 3.

Plate XXIV—Change "XXII" to "XXIII".

Plate XXX—To *A* add (See Plates XXIII and XXIV).

Plate magnifications: 20 times—Plate XII *A*; 200 times—Plates V, VI, XI *A*, XIII *A*, XIV *A*, XV and XVII; 1000 times—Plates XI *B*, XII *B*, XIII *B*, XIV *B*, XVI *A*, XXI, XXII, XXIV, XXVIII, XXIX, XXX, XXXI, and XXXII.

Page 25, 3rd and 4th lines from bottom—Change "600 to 700" to "60 to 70", and "50 to 100" to "5 to 10".

CORRELATION OF COAL BEDS IN THE MONONGAHELA FORMATION OF OHIO, PENNSYLVANIA, AND WEST VIRGINIA.

By REINHARDT THIESSEN *and* J. N. STAUD.

INTRODUCTION.

The geologist is not always readily able to correlate with the correct horizon of the geological system the coal outcrops or coal beds penetrated by drill-holes, or even the coal being worked in certain mines. This is particularly true in areas that have been subjected to extensive erosion, and are now cut by ravines and drainage systems. When faults occur in such areas the problem becomes still more complex.

In the deeper seated coal beds, where drilling is the only means of finding them, it also becomes difficult at times to correlate with the correct geological horizon the coal bed penetrated.

The greatest confusion, however, arises from the fact that in earlier days, coal beds all over the country were given local names without reference whatever to the same coal in other localities. Such names generally were given after the name of the town, township, county, or streams in or near which they were found. For example: the Redstone bed was so named after a creek by that name near which it was found. The Sewickley bed was also named after a creek nearby. In other places these same beds are called by other names, such as Pomeroy for Redstone, and Mapletown for Sewickley. It thus happens that certain beds have received a number of names. For example: the lower Kittanning today is called the "B" seam, the Sonman, Black Lick, and Dagus in different localities. This is more or less true of all the beds. It may be readily seen that the names of all the coal beds taken together have become numerous. To this confusion, the geologists from the earliest days have contributed their part to make the matter even worse. In Pennsylvania, J. P. Lesley, as early as 1840 inaugurated a system in Cambria county, in which the beds were designated by letters (A, B, C, D, etc.) from the lowest beds then known upwards. Concerning this mistake, Lesley himself writes[1]:

> It is my duty to add here that it was most unfortunate that in 1840 I persuaded my friend and colleague, J. T. Hodge, to letter our principal coal beds in Cambria and Somerset counties from the bottom upwards, A, B, C, D, E, and that in the rapid survey of northern Pennsylvania, which I ordered to be made in 1841, through Tioga, Bradford, Potter, McKean, Jefferson, Clarion, and Armstrong counties, as far south as Freeport, I employed this same lettering for my imaginary identification of the coal beds there.
>
> My unadvised adoption of this imperfect and erroneous nomenclature in my Coal Manual in 1857 has embarrassed subsequent surveys, and introduced confusion into the nomenclature of the Reports of Progress of 1875, 1876, and 1877.
>
> This boyish nomenclature has crept into our literature and has been a hindrance to broad views of our carboniferous geology. Indefinite in its very nature, but with a pretentious claim to extra definiteness, it has been necessarily misquoted by more than one author, owing to an inadequacy of data for deciding which was lettered A, which B, etc.

In Ohio, the earlier geologists started a system of nomenclature, beginning with No. 1 for the lowest known bed, and proceeding numerically upwards with the higher beds. To make matters worse, not all of the beds had been discovered when the system was begun, and those beds discovered later had to be designated by adding a subscript to the number in the series in which they occurred. For example: 6b was given to the lower Freeport bed, and 6a to the upper Kittanning, etc.

In the field work of procuring samples and visiting various mines, much information was gathered by conversation with the miners, and every trip seemed to add to the complexity of correlation. There seems to be no definite name assigned to any one bed in this entire region. From all possible sources the local names of the beds have been obtained and given here.

ACKNOWLEDGMENTS.

Thanks are due to the mine owners, superintendents, and miners at the various mines visited, which are mentioned later. The manuscript was read by J. W. Paul, chief coal-mining engineer of the Bureau of Mines; H. N. Eavenson, of Pittsburgh; also by G. H. Ashley and J. D. Sisler, state geologist and associate geologist, respectively, for Pennsylvania; J. A. Bownocker, state geologist

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[1] White, I. C., The Geology of Lawrence County, 1877, vol. QQ, p. 29 of preface, by J. P. Lesley.

for Ohio; and I. C. White, state geologist for West Virginia. Thanks are also due for the suggestions made, which have been incorporated herein.

MONONGAHELA SERIES.

Waynesburg bed.—In Pennsylvania and Ohio this is known as the Waynesburg, but in the latter state it is also known as No. 8b, No. 11, and Macksburg.

Sewickley bed.—In Pennsylvania this is known as the Sewickley, the Mapletown, and the Four Foot; while in Ohio it has been named the Meigs Creek, and No. 9.

Redstone bed.—In Pennsylvania this is known as Redstone, but in Ohio it has been termed the Pomeroy or No. 8a.

Pittsburgh bed.—In Pennsylvania this is known as the Pittsburgh, River Vein and Nine Foot; in Ohio it is called Pittsburgh, No. 8, Federal Creek, and Swan Creek; and in West Virginia it is called Pittsburgh, Elk Garden in a small area, and other names.

ALLEGHENY SERIES.

Upper Freeport bed.—In Pennsylvania this has been called "E" seam, Lemon, Coke Yard, Kelly, Sawmill, Four Foot, and Five Foot; while in Ohio it has been named No. 7, Black Band, Big Vein, Del Ray, Sherrodsville, Cambridge, Alexander, Blue Rock, Bayley's Run, Norris, and Waterloo.

Lower Freeport bed.—In Pennsylvania this has been called "D" seam, Moshanon, Limestone, Shantz; while in Ohio it has been named No. 6a, Roger, Whan, Steubenville Shaft, Randen Furnace, and Hatcher coal.

Upper Kittanning bed.—In Pennsylvania this is called "C" prime, Darlington, N. Washington cannel, Woodland, Big Bed, Cement, Rock Vein, and No. 4 Creek Vein; while in Ohio it is wanting.

Middle Kittanning bed.—In Pennsylvania this bed is only known by that name and "C" seam; while in Ohio it has been named No. 6, Osnaburg, Coshocton, Upper Zanesville, Upper New Lexington, Nelsonville, Straitsville, Great Vein, Carbondale, Mineral City, Upper Zaleskie, Washington Furnace, Block Bed, Hammondville Strip Bed, Dry Run Coal, and Sheridan.

Lower Kittanning bed.—In Pennsylvania this has been named "B" seam, Miller, Sonman, Black Lick, Dagus, Bloss and Barnott; while in Ohio this same seam has been called No. 5, Leetonia, Creek Vein, Hammondville, Potter's Vein, Clay Vein, Mineral Point, Lower New Lexington, and New Castle coal.

Clarion bed.—In Pennsylvania this has been called "A" prime, Fulton, Pardee, Clermont, and Scrubgrass; while in Ohio it has been termed Clarion No. 4a.

Brookville bed.—In Pennsylvania this has been called "A" seam, Cushman, Seymour; while in Ohio it is known as No. 4, Gray Limestone, Winter's, Flint Run, and Conway coal.

POTTSVILLE SERIES.

In Pennsylvania the Mercer coals are known as Upper and Lower Mercers, Upper and Lower Alton, Mt. Savage, Gaines, "B"; Bear Creek, and "A" seam. In Ohio the Pottsville is divided into the Tionesta—known as No. 3b, Wartman, and Bolivar; Upper Mercer—known as 3a, Bedford Cannel, Strawbridge Cannel; Lower Mercer—known as No. 3, Wilbur, Flint Ridge and No. 2; Quakertown—known as No. 2, Wellston, Jackson Hill; and Sharon—known as No. 1, Palmyra, Mahoning, Brier Hill, Massillon, Wadsworth and Jackson Shaft coal.

In West Virginia there are over 21 coal beds in the Pottsville formation, grouped in three divisions, the upper one being called the Kanawha group; the middle, the New River group; and the lower, the Pocohontas group. Each of these beds has at least one local name, in addition to more names in other localities in that State.

The Kanawha group includes the Stockton-Lewiston, also known as Big Bed and Belmont seam; the Coalburg, also known as Twin seam, Buffalo Creek; the Winifrede, known as Black Band, Dorothy and Quakertown; Chilton seam; Cedar Grove, also called Island Creek, Red Jacket, and Thacker; Alma, also called Peerless; No. 2 Gas, also called Campbell Creek, Upper War Eagle, Freeburn, Burnwell, Rawl, and Warfield; the Powelton seam; and Eagle seam, also known as No. 1 Gas, Middle War Eagle, and Mohawk.

The New River group includes the Iaeger, known as "B" coal, Sewell, also known as Davy; Welch, also known as Tug River; Beckley, also called War Creek; and Fire Creek, also named Quinnimont.

The Lower Pottsville or the Pocohontas group consists of the Little Fire Creek and mine beds numbered from 1 to 9, and three beds below No. 1.

WHY COAL BEDS SHOULD BE CORRELATED.

Partly on account of this confusion of names and misinformation, and partly for other reasons, there is a wide lack of knowledge among the various classes of men employed in the coal industry as to the identity of the coal bed in which they are working—the coal they are mining is often not at all what they designate it. Occasionally the misnaming of a coal bed is intentional. A coal from a certain bed and from a certain mine may naturally have been dirty, or through carelessness or otherwise in mining it may have contained much dirt and bone, and thus come into disrepute. This same coal is later bought on the market under a name other than the correct one. Or, certain operators knowing that a coal has a poor reputation, sell their coal from the start under a name other than the correct one. Thus the coal buyer is at the mercy of the seller and the miner as to the kind of coal he is receiving, and he has as yet no method by which he can tell from which bed the coal is mined.

The man who buys or leases coal lands or coal beds has in certain cases no reliable data to correlate the bed he considers buying or leasing, and has no absolute check on the correct name of that bed. In certain parts of Ohio for example, the buyers or leasees of coal land are so uncertain about the name of the bed in question, that in order to be safe, they insert in the contract or lease the distance of said bed above or below certain well-defined geologic formations, such as the Ames limestone or the Berea sandstone.

If a method could be devised by means of which, through certain characteristics of the coal or certain constituents in the coal, it could be identified, a great aid would be rendered to those concerned.

It has been known for some time that certain coal beds have certain characters or contain certain constituents characteristic to that bed, and not found in any other bed[2]. The spore-exines (see page 15 for definition) in particular have definite and clearly defined characteristics—such as form, size, and sculpturing—by means of which different kinds may be distinguished from one another. In the coals, the characteristics of these ancient spores have in many cases been so well preserved that one species can easily be distinguished from other species. In examining the spore-exines of a number of sections of a certain bed it was found that by far the larger number of the spore-exines of that bed are largely of the same kind. In other beds, two kinds; while in others, three kinds of spore-exines form the bulk of the spore matter. In comparing the predominating spores of one bed with those of another, it was found that those of one bed are different from those of any other. Although comparatively few beds have been examined in this respect, there was sufficient basis to believe that each coal bed, or at least many coal seams, contains one or more spores which are predominant and characteristic of that bed. Based on this principle, it appeared possible to identify a coal by means of such characteristics. It was therefore thought important enough to pursue a systematic investigation to either prove or disprove the feasibility of correlating coal beds by this scheme.

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[2] Structure in paleozoic bituminous coals, by Reinhardt Thiessen, Bull. 117, Bureau of Mines, 1920, 250 pp.

The main coal beds of the Monongahela formation—namely, the Pittsburgh, the Redstone, and the Sewickley—were selected for this work.

THE PITTSBURGH BED.

This bed was named "Pittsburgh" by Messrs. McKinly, Jackson, and other assistants of Prof. Rogers[8] in 1836-1840, and was traced by them from Pittsburgh to Connellsville; and by Jackson from Connellsville southward to the Virginia line, and back along the Monongahela River to Pittsburgh; and northward to New Alexandria, Blairsville, and Saltsburg, through northern Westmoreland County to Pittsburgh. The early coal men in the Connellsville region had imagined that the bed there was a different one from that at Pittsburgh.

The Pittsburgh bed extends west and southwestward from Pittsburgh to the middle of West Virginia for a distance of over 125 miles, where it covers almost one million acres in the counties of Brooks, Ohio, Marshall, Wetzel, Marion, Harrison, Monongahela, Tyler, Doddridge, and small portions of a few others; on the west it extends into eastern Ohio, covering almost the whole of Belmont County, and parts of Guernsey, Noble, and Monroe counties; on the east it has development in Maryland and the

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[8] Second Geological Survey of Pennsylvania, vol. L, 1875, pp. 1-2.

Upper Potomac Valley of West Virginia, where it has been an important production factor for the past fifty years. It reaches its thickest development in the Georges Creek Valley of Maryland and Elk Garden district of West Virginia. West of Chestnut Ridge in Southwestern Pennsylvania, especially in Greene County, where the reserve of this coal has been estimated by the State Topographic and Geologic Survey[11] as 2,831,453,000 tons. This area, with certain wants, is a continuous sheet from Pittsburgh south through the upper half of West Virginia into Virginia and Maryland, including portions of Ohio along the Ohio River. There are a few outlying basins not included in this enormous area, such as in Indiana and Somerset counties, Pennsylvania, and Barbour, Mason, Gilmer, Taylor, and Putnam counties, West Virginia.

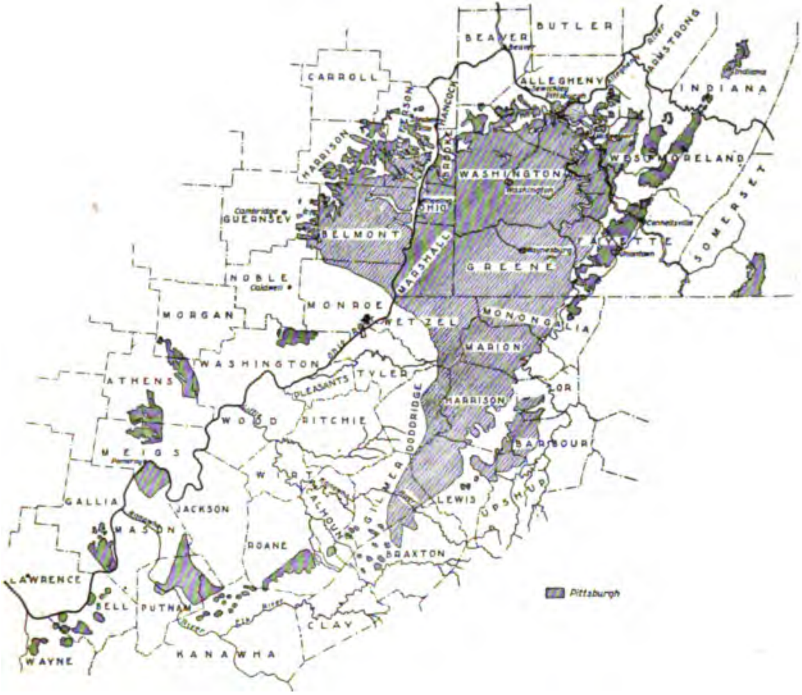

Figure 1.—*Map showing area underlain by Pittsburgh bed.*

It has been estimated that the original area underlain by the Pittsburgh bed covered 90,000 square miles, but erosion and denudation has carried away the larger part. Yet the Pittsburgh region has suffered less in this action than any other part of the

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[11] Coal reserves of Greene County, Pa., by John F. Reese: Bull. 25, State Topographic and Geologic Survey, 1922, 6 pp.

State. At present[4], the Pittsburgh bed is reported to underlie 2126 square miles, averaging 7 feet in thickness in Pennsylvania: 2609 square miles and 7 to 9 feet thickness in West Virginia; and to be equally thick over 1590 square miles in Ohio. The areas of the bed in the last two mentioned States are considered probably overstated by the writers quoted. Figure 1 shows the area underlain by the Pittsburgh bed.

Starting at the east of the Pittsburgh area, the Pittsburgh coal has a fuel ratio[5] of 3 to 4. (By fuel ratio is meant the ratio of fixed carbon to volatile matter.) Coming westward to Ligonier, east of Chestnut Ridge, the fuel ratio is from 2 to 3; crossing this ridge into the Connellsville region the ratio drops to about 2. Crossing the Fayette anticline the fuel ratio averages 1.5 to 2. Going into Greene county across the Monongahela River the fuel ratio will still average about 1.7 or 1.6. This value will also hold for southeastern Washington county.

CHARACTERISTICS OF PITTSBURGH BED.

The Pittsburgh bed is underlain by the Conemaugh formation, and rests upon an uneven floor of fireclay, which seems to be persistent, but varies in physical characteristics. In some places it is soft and plastic, while in others it is hard and flinty. Above the coal is the Pittsburgh sandstone member ranging from 0 to 30 feet in thickness; and between this and the coal bed there is always a thin layer of gray shale of varying thickness. On exposure to air it crumbles readily, so that considerable timbering is needed in mines having much of this shale.

The Pittsburgh bed proper may be considered to consist of two parts—namely, (1) a roof coal, and (2) the worked coal, separated by the main clay parting.

In the roof there are several seams termed "riders" or "roosters," varying in number from 2 to 8. In the Experimental Mine of the Bureau of Mines at Bruceton, Pa., there are two rather characteristic riders, while in the Francis mine at Burgettstown there are a varying number of rooster or rider seams, which vary in thickness from several inches to 8 feet. Here the main bed is mined first, and the clay parting separating the main bed from the riders several feet thick, is caved on the floor, and tracks are laid again upon this caved material, which serves as a floor for the mining of the rooster seams. The draw-slate is taken from the coal in the mine and is placed in the gob. The roof coal as well as the rider coal presents a dull luster and tarry appearance, with a smooth surface and greasy feel. It usually contains a high percentage of ash, and in the Pittsburgh region it shows a characteristic cubical cleavage and laminated structure.

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[4] The origin of coal, by David White, Reinhardt Thiessen, and C. A. Davis: Bull. 38, Bureau of Mines, 1913, p. 35.

[5] Report of Topog. and Geol. Survey Com. of Pennsylvania, 1906-1908, p. 229.

The main bed shows several bone partings which divide this portion into at least three benches—namely, the Breast coal on top, the Bearing-In coal, and Brick coal at the bottom. There is, however, no sharp dividing line between these, the one gradually merging into the other.

The clay parting lies above the upper part of the Breast coal, which, when removed, exposes the draw-slate, and this must be taken down, and the roof coal then supports the overlying material and forms a durable roof. This part is usually the thickest part of the bed, and generally contains the best coal.

The Bearing-In coal rarely runs over 4 to 6 inches in thickness. It has been given this name because the pick miner works in on this portion to get a free face against which to bring out the other parts of the bed. Nearly all pick miners are well acquainted with this practice, and readily point out this part of the seam to all visitors. Some miners have learned to correlate one mine with another simply by noting this Bearing-In coal as being present in both mines, so that if the one were Pittsburgh coal, then the other would be the same coal. The one drawback in this coal is that this part of the bed shatters readily and forms slack.

The Brick coal below the Bearing-In coal takes its name from the angular sizes and shapes into which it breaks when mined. These lumps resemble common building brick, so that the term "brick" coal has been applied by the miner. In many of the mines this coal is likely to contain a large amount of clay and pyrite. Some machine miners set the cutters so that the pyrite and clay are avoided

The bottom division, or, as it is commonly called, the floor coal, is that portion of the mine upon which the tracks are laid, and it acts as a floor in the mine. This coal is rarely mined and sold on a large scale because it is so high in ash and mineral matter. There is always present a pyritiferous binder between the brick coal and the floor coal. The water in the mine, if at all present, readily gains an entrance into the mine by coming in at this binder; so in order to keep the mine as dry as possible by natural means, this portion is left there, and the cutters are so arranged that about 5 or 6 inches of floor coal remain unmined. In some cases more floor coal has to be left in the mine, because the fireclay under the floor causes creeps and squeezes, thus damaging the mine.

All of the beds of the Monongahela formation are underlain by fireclay. When taking the fireclay, about 6 or 8 inches below the coal is found to consist of a clayey kaolin, and contains a wide assortment of such minerals as disintegrated feldspars, microcline with its "gridiron structure", quartz, tourmaline, the mica group, zircon, apatite, magnetite, etc. There may also be seen in this fireclay at this horizon a small quantity of bituminous substances. Going upwards from this point the same kind of minerals persist, but the bituminous material increases. This increase in bituminous matter grows as the bed is approached. Thin coal-like strips soon appear, becoming numerous and thicker, until pure bituminous coal is reached at the bottom of the bed.

The designations "roof coal" and "floor coal" are flexible terms, and are not really understood in technical parlance today as well as they should be. Floor coal means that the coal used as a floor in a mine serves only in that capacity, and is lost to future mining. In the same way, roof coal means that coal serves as a protective covering in a mine, and in playing this role takes the place of expensive timbering, and is also lost to future mining. The coal itself may not differ from the other coal.

The floor in any mine, as well as the roof, does not have to be of coal. It may be limestone, sandstone, or shale. The main idea in coal mining is to get the largest amount of coal from the mine with the least expenditure, and the two pre-requisites for this are a good solid floor and a substantial roof.

The roof coal of the Pittsburgh bed is of rather different structure than the main coal, being higher in ash and mineral matter. Overlying this in a number of mines are other smaller stringers or thin seams of coal similar to the Pittsburgh bed coal. These have been named "rooster seams," "riders," and "stringers." In the Francis mine at Burgettstown, Pennsylvania, the total thickness of these rider seams is about the same as the seam proper. All of this coal was mined and sold on the markets for steam and domestic purposes. In the Experimental Mine of the Bureau of

Mines, as already stated, there are two rider seams of minable thickness, but the intervening sandstone makes mining costs too excessive.

In Pennsylvania, the Pittsburgh bed shows a variation in thickness from 4 to 16 feet; in Ohio it varies from 2 to 6 feet; in Maryland it averages about 8 feet, although in one place in the Georges Creek basin it attains a thickness of 22 feet; and in West Virginia, it varies from 7 to 9 feet. Throughout this large area it is remarkable for its uniformity, structure, quality, and like characteristics.

THE REDSTONE BED.

The earliest records in Pennsylvania of the Redstone bed are dated 1759, when the coal was used by Col. James Burd on his campfire[6]. The coal was taken from the bank along the Redstone Creek, Fayette County, Pennsylvania, near Coal Run on the Monongahela River, near the present site of Brownsville.

In Meigs County, Ohio, the coal was found as early as 1876 at an elevation of more than 100 feet in the face of the river hills 12 miles above the mouth of the Kanawha River, and 2 miles below the mouth of Leading Creek[7]. It is also abundant on the West Virginia side or left bank of the Ohio River, opposite to this deposit, and is without doubt a continuation of the second bed found on the Kanawha. It is of the same thickness as at Pomeroy. Above the coal is a deposit of shale and ash-colored marly clay, 8 or 10 feet thick, which forms the roof of the mine. The coal deposits are thin and scarce near the Ohio River from the mouth of Pipe Creek, 15 miles below Wheeling, to Carr's Run. As the coal dips under the river, at both these places it can be reached only by shafts.

In the mines visited by the authors of this bulletin, the Redstone bed in its best development reaches a thickness of from 50 to 55 inches. It consists of a lower and an upper bench, with a thin floor coal under it and a slightly thicker roof coal above it. In many places it is friable and will not stand shipment, but is a good domestic fuel. The bed is separated by frequent clay partings. The coal contains a large quantity of kaolin, quartz, and disintegrated feldspars, which makes a high ash content, and hence make it a poor coal for some purposes.

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[6] Pittsburgh Commercial Gazette, July 29, 1886.

[7] Silliman's Journal, vol. 29, 1876, p. 51.

The bed is overlain by a sandstone averaging from 60 to 70 feet in thickness, which serves as an ideal roof, and also permits of the roof coal being mined and sold with the main coal. The roof coal seldom reaches a greater thickness than 3 or 4 inches. Underneath the bed there is a soft fireclay, which necessitates the leaving of a rather thick strip of bottom coal as a floor in the mine.

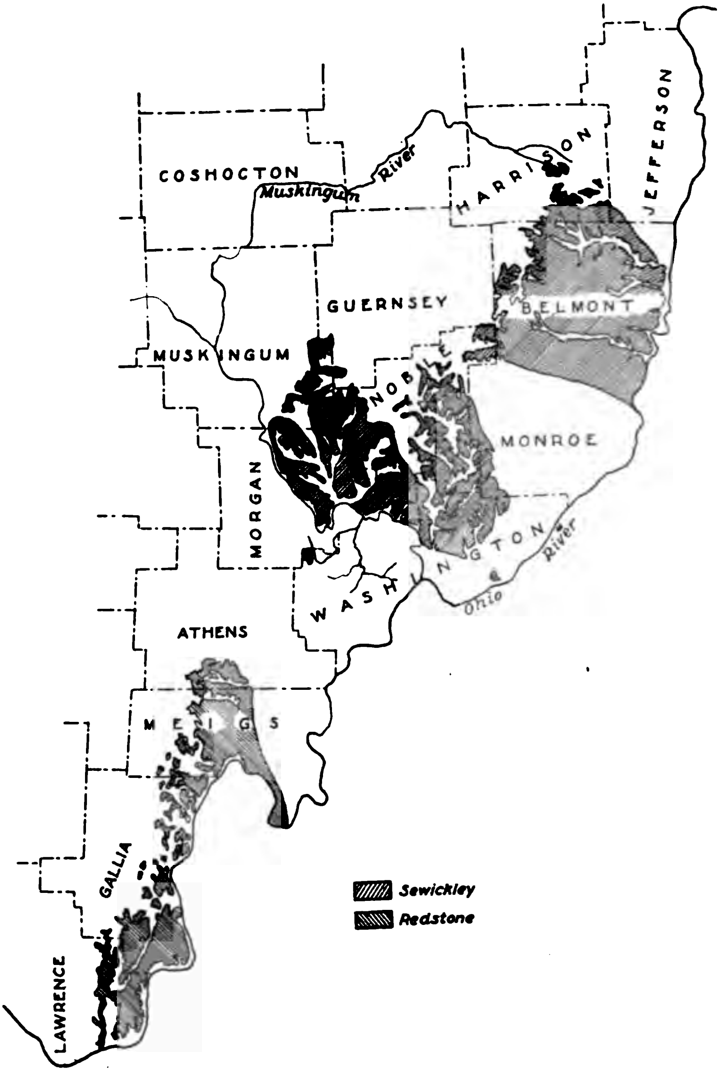

FIGURE 2.—*Map showing area underlain by the Sewickley and Redstone beds.*

In Pennsylvania, the Redstone bed averages from 0 to 5½ feet in thickness, and in many places it is too thin to mine at present. In Ohio, it reaches its best development in the southern part of the State (See Figure 2) there becoming an important mining section. In West Virginia, it varies from 4 to 6 feet in thickness, and is noted for its excellent characteristic sandstone roof.

THE SEWICKLEY BED.

The Sewickley coal bed is first mentioned in the Second Geological Survey of Pennsylvania in a Report of Progress in Fayette and Westmoreland counties in 1875 and 1876. It attains its chief importance in the southeastern part of Greene County, being too thin elsewhere to be of any value. It has been traced along the Mononghela River to the Washington County line by J. J. Stevenson. In the northern part of Fayette County it is frequently a bituminous shale, and at numerous localities it seems to be wholly absent. In Allegheny County it could not be identified.

South of the village of Madison, Pa., in the hill, the Sewickley coal is seen and recognized by its "blossom" (decomposed outcrop). Following this outcrop down the Big Sewickley creek the bed is well exposed at about ¼ mile above Bell's Mill, where it consists of a richly carbonaceous shale measuring 30 inches in thickness[8]. The coal in the Youghiogheny River districts lies evenly for the most part, and gives no trouble in mining.

The Sewickley bed, as far as examined in its best development, ranges from 50 to 66 inches in thickness. It is underlain by a soft fireclay and overlain by a thick sandstone layer. Throughout the bed there are numerous clay partings, which raise the ash content and lower the heating value of the coal.

The bed proper is usually divided by clay partings into a lower bench, a breast coal, and an upper bench. The best coal comes from the breast coal, and is 10 to 14 inches in thickness. The pick miner begins on this coal, and in this respect it resembles the Bearing-In coal of the Pittsburgh bed.

The roof coal is thin in most mines in the Sewickley bed, and is taken down with the bed and sold as domestic coal. Only when the mineral matter and clay appear to be above the average is the roof not loaded, but is thrown back into the gob.

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[8] Report of Progress in Fayette and Westmoreland Counties, Second Geol. Survey of Pennsylvania, 1876, p. 353.

As a comparison of the bed coal and the roof coal, analyses may be cited. These samples were taken at the Hays mine, Newcomerstown, Pennsylvania.

Comparison of analyses of main coal and roof coal.

Constituent	BREAST COAL.			ROOF COAL.		
	Coal as received.	Moisture free.	Moisture and ash free.	Coal as received.	Moisture free.	Moisture and ash free.
Moisture	0.5	......	......	0.6	......	......
Volatile matter	35.5	35.6	40.8	37.3	37.5	42.5
Fixed carbon	51.4	51.8	59.1	50.3	50.7	57.5
Ash	12.6	11.6	......	11.8	11.8	......
Sulphur	4.6	4.6	5.2	2.3	2.3	2.6
B. t. u.	13240	13300	15230	13380	13450	15250

The sample of breast coal was considered by the mine owners to be their best coal. The roof sample was taken at the same place in the entry directly over the same coal. It will be seen from this, that for domestic purposes there is no particular difference between the roof and the breast coal. As long as it passes the eye of the miner, the coal is good for home fuel consumption.

One outstanding feature of the Sewickley bed is the abundance of kaolin and sericitic mica. These two minerals seem to be persistent throughout the entire bed. While pyrite is also abundant, it rather confines itself to the clay partings separating the coal into benches.

In Pennsylvania, the Sewickley bed averages about 3½ feet in thickness, and improves in composition and thickness in West Virginia along Scotts Run, where it is 6 feet in thickness. In Ohio it is rather variable, ranging from 2 feet upwards; but in its best condition in Belmont and Harrison counties it averages about 4½ feet (See Figure 2). The floor and roof of this bed are rather irregular, rising and falling sharply in short distances, thus increasing or decreasing the thickness of the coal. In some cases the roof dips so sharply that the coal may disappear entirely. In Belmont County, Ohio, a thick bone coal appears in this bed in varying thicknesses from several inches to 3 feet.

ORGANIC COMPOSITION OF COAL.

SPORE-EXINES.

Every coal contains a smaller or larger number of spore-exines as part of its composition, and as they are the main constituents that furnish characteristic marks for the identification of a particular bed, it is essential to know what they are.

Spore-exines are merely the shells, or outer walls, or coverings of spores. The easiest way to illustrate what spores are is to refer to the ordinary ferns, so often grown in pots as house plants. On the under surface of the leaves of the ferns, rows of dots are visible at most any time of the year. When the fern is handled at certain periods a fine dust is seen to come off the leaves having these spots. This dust consists of the spores of the fern. Unfortunately, ferns of this type did not contribute materially to the coal flora of the Carboniferous Age, and therefore furnish a poor example as to the kind of plants contributing to coals.

The common horsetail or *Equisetum,* and the club moss or *Lycopodium,* of both of which there are a number of species, and which are direct descendants of plants that contribute largely, if not the most, to the coal substances, are much better examples to illustrate the origin of spores in coals as well as the main or woody and other substances in coal.

The present common horsetails (See Plate I) are the lingering remnants of the Calamites, a once abundant vegetation which largely contributed to coal. Horsetails grow in moist or in dry places, sometimes in great abundance. Early in the Spring a slender stalk shoots up from a slender rhizome, bearing on the end a club-shaped shoot (*1* of Plate I). This is the spore-bearing part of the commonest of the horsetails, *Equisetum arvense.* Soon a large amount of yellow powder may be seen to come off this cone when lightly touched. This yellow dust again consists of the spores (*6* and *7* of Plate I, and *c* and *d* of Plate II). In a short time these spores are all shed and the stalk again disappears, shortly to be followed by other shoots which develop into small tree-like or bushy plants (*2* of Plate I). These are the plants of the horsetail as ordinarily known, and do the chlorophyl work of the plant.

When the early shoot is examined a little more closely it will be found to consist of a slender stalk with a number of whorls of sharp scales one above the other, and ending in the thicker club-shaped cone. On close examination it is found that the surface is divided into hexagonal areas, which are the outer ends or shields of so many sporophylls (*a* of Plate II). When these are carefully removed and examined with the aid of a magnifying lens, it will be seen that underneath the hexagonal areas there are 6 to 9 long "sacks," the sporangia, (See *3* and *4* of Plate I and *a* and *b* of Plate II) each filled with hundreds of spores. (See *6* and *7* of Plate I and *a, c,* and *d* of Plate *II*). The botanists call these "asexual spores." When these fall on wet soil they will germinate and form a small, green, insignificant tuberous plant called a "prothallium," which is designated by botanists as the "sexual plant," or gametophyte. It is so small and insignificant and short-lived that it will evade ordinary observation. In fact, ordinarily, it is but rarely found. On the prothallia develop two kinds of sex organs—namely, archigonia and antheridia. In each archigonium a single egg is developed, while in each antheridium a number of sperms are developed. When mature, and under favorable conditions in the presence of water, the sperms will swarm and swim over to the archegonia. One finds its way to each egg, and unites with it. The egg is then said to be fertilized. The fertilized egg or oospore will now germinate and grow into the second or asexual generation of the life cycle of the plant, also called the sporophyte. This is the plant with which we started out, and from which the early shoots arise above the ground with the cone crowded full of spores, and later to be followed by the small tree-like green plant.

The *Lycopodia,* popularly known by the name of "club mosses," and whose ancestors, the *Lepidodendrons,* also contributed largely to the coals, are good examples to illustrate what is meant by microspores and megaspores.

Club mosses, also called ground pines, are small tree-like or bushy plants, hardly more than a foot high, although their ancestors during the Carboniferous times grew to large trees. The stems and branches are clothed with small leaves, having a moss-like appearance. Often the erect branches are terminated by conspicuous cones. (See Plate III.) These cones have the appearance of clubs, and from that and their moss-like appearance they get the name of club mosses. The cone, it is seen, consists of thick and closely overlapping leaves. These are the sporophylls (*A* of Plate IV.) On the underside of each of these is a globular sack, the sporangium (*B*) each filled with thousands of spores (*C* and *D*). It is the source of the lycopodium powder used for various purposes and for sale in drug stores. The life cycle of the Lycopodia is similar to that of the horsetails. The spores germinate and form prothalia or gametophytes; the gametophytes develop archigonia and antheridia; the archigonia develop eggs, and the antheridia develop sperms, which, under favorable conditions swarm and gain an entrance to the egg, which it fertilizes. The fertilized egg germinates and develops into the sporophyte, or Lycopodium plant as it is generally known. In these cases the spores are all of the same size, and small, and are usually designated by the term of "microspores." There are found in the coals certain large spores called "megaspores." The origin of the megaspores is well illustrated in some of the Lycopodiales, particularly in the genus *Selaginella,* which grows in warmer climates, and is locally only found in the greenhouses. Although more delicate, it looks very much like Lycopodium. Certain terminal branches bear cones just as Lycopodium; but the important difference is that the sporophylls in the upper part of the cone, bear, as in Lycopodium, numerous small or microspores, while the sporophylls in the lower part of the cones each bear only four large or megaspores.

When the megaspores germinate they form gametophytes, which develop archegonia only, and hence eggs only are formed; while when the microspores of the same cone germinate, they form gametophytes, which develop antheridia, which will develop sperms only. The sperms, as in the other cases, fertilize the egg developed from the megaspore. The fertilized egg again develops the asexual or sporophytic plant seen in greenhouses.

In the Lycopodiales, the gametophytes are so small that they do not even leave the shell of the spores. In the last stages of the development of the spores, the last two divisions of the mother cells occurs simultaneously, giving rise to four cells which develop together into four mature spores, and are therefore called "tetraspores." This position in fours lends each spore a characteristic triradiate mark, called the "tetrasporic mark," which identifies it as a spore. Every spore consists of the living or protoplasmic part, which is enclosed by a thin membrane, the entine. The whole is covered by a thick-walled outer wall or exine. The protoplasmic or living part decays readily, and contributes nothing, or at the most but little, to the coals. On the other hand, the outer walls or exines are composed of resistant substances like waxes, oils, and cutocellulose, and withstand all the coal-forming processes, persist well preserved in the coals, and have contributed a considerable part to them. In the Carboniferous Period the coal-forming plants consisted largely of *Lycopodiales,* represented mainly by the Lepidodendrons, Bathrodendrons, and Sigilaria;

and *Equisetales*, represented by the Calamites, of which there was a large list of families, species, and sub-species. All of these bore spores similar to those cited as illustrations. Some of them must have shed an enormous amount of spore matter every year. Although the spore matter in coals is only represented by the outer wall or exine, it will be referred to as spores instead of spore-exines in this paper.

As in the Lycopods and horsetails of today, the spores of their ancestors differed from each other in species and families in certain respects such as sculpturing, form, size, and thickness of spore-wall, by means of which they may be distinguished from one another.

In must be considered that each coal bed was a large swamp some time in the Carbonferous Period, and that each swamp embraced a society of plants all growing under similar conditions. As is the case today, only a few species of plants grow together under similar conditions, so in the Paloeozoic times it appears that only a few species grew together under similar conditions. It also must be remembered that the different coal beds are separated by very long time intervals, and that during those periods the conditions probably changed more or less, and the plant societies had time to change, one species being replaced by another, or species themselves had time to change in order to adapt themselves to new conditions.

Since conditions were not repeated alike, different species predominated at different periods, or even different families predominated at the different periods in which the coal bed was formed. We arrive at this conclusion from a study of plant societies of today, also from the fact that each coal bed reveals certain spores and certain types of plant remains which predominate throughout a certain bed, but are either entirely absent in any other bed or are found but sparingly in other beds. Again, other spores, although not numerous nor predominant, are only found in a certain bed and not at all in any other bed. This all indicates that the plant societies consisted of but a few species. It also stands to reason that if a flora consists predominantly of two or a few types of plants, not only the spores but also the coal substance itself, and the attritus other than spores resulting from the accumulation of such a flora should differ from the debris of flora consisting of a different or different types of plants. And by observation it is found that such is the case.

It should therefore not be difficult to find enough characters in each coal bed by means of which to distinguish it from any other. The spore-exines furnish the best characteristics by means of which this can be done.

CORRELATION CHARACTERS OF COALS IN THE MONONGAHELA FORMATION.

Three coal beds of the Monongahela formation—namely, the Pittsburgh, the Redstone, and the Sewickley beds—were examined systematically for correlation characters, which were studied from widely separated and fairly well-distributed localities in these beds. The coals were examined at the following mines and localities:

Localities where the coal beds were studied.

Bed	Mine	Place	State
Pittsburgh	Edna	Irwin	Pennsylvania
Pittsburgh	Francis	Burgettstown	Pennsylvania
Pittsburgh	Experimental Mine of Bureau of Mines	Bruceton	Pennsylvania
Pittsburgh	Keystone	Madison	Pennsylvania
Pittsburgh	Randall	Randall	West Virginia
Pittsburgh	Rosemary	Flushing	Ohio
Pittsburgh	Beach Bottom	Short Creek	West Virginia
Redstone	Betty	Madison	Pennsylvania
Redstone	Hays	Hays	Pennsylvania
Redstone	McKitterick	Pomeroy	Ohio
Sewickley	Belmont	Flushing	Ohio
Sewickley	Freda	Caldwell	Ohio
Sewickley	Jarvis	Randall	Pennsylvania
Sewickley	Swancy No. 1	Fairchance	West Virginia

Every coal so far examined contains spores. Some coals contain large numbers of them as in the Pittsburgh bed, while others contain relatively few. Both the Redstone and the Sewickley beds are examples of coals of low spore content.

In a cross section of the coal, the spores, if not broken, appear as flattened rings. In their original form, spores are spherical; but in the process of coal formation, when pressure was brought to bear on them, the spheres were pressed flat. Much of the spore matter was broken and even macerated, and when in this form it is of little value as identifying characters of the coal. In a horizontal section of the coal the whole spores appear as circular discs—some tending to be triangular, others oval. They are of a clear light-yellow color, and transparent in thin sections, becoming brownish-yellow in thicker sections, and are conspicuous objects in coal under magnification.

The spores may be separated out of the coal by digesting the coal with Schulze's reagent, and subsequently treating with dilute ammonia. The ordinary coal substance will dissolve, while the spores and cuticles, together with some other substances, will come out undissolved. The spores may then be studied under the microscope, and all of their characters examined in detail. When thus examined, together with their appearance in cross and horizontal sections, the characters can generally be determined well enough, provided that the spore itself has not suffered too much through the coal-forming agencies or subsequent metamorphism.

Frequently spores are found, in some coals more than in others and in the same bed in certain horizons more than in others, which have been effaced of much or even all of their characteristics. Such spores are useless for identification purposes. It also happens that the spores in a certain section are all in a good state of preservation, and in the section immediately next to it are so poorly preserved as to be utterly valueless.

In order that a spore be of use as an identifying medium in a coal it must have definite and specific characters by means of which it may easily be recognizable, and must be present in a bed in sufficient numbers and distributed throughout the whole bed; and to be of the greatest value it should not recur in any other bed or in but small numbers in more than one bed. It is, however, not absolutely necessary not to recur in other beds to be of value.

The number of the spores in the coal also furnish valuable data for identification purposes. In this relationship it is important that the number of spores as a whole be considered, and not in haphazard sections or horizons. As far as the coals have been examined it is the rule that the number of spores increases from the bottom up, no matter how many spores there may be in the coal as a whole. The total amount of spore matter in the first few inches—in some beds through the first few feet—is small, and becomes more and more abundant towards the roof, so that there is always a great difference in the relative number of spores at the bottom and at the top of the bed. And again, certain thin layers may contain a relatively large number of them, so that a section made from it would indicate that the coal was composed largely of spore matter, while a layer just below or immediately above it may contain but relatively few spores. Yet the total amount of spore matter in one bed as a whole may differ very much from that of another, as is the case in the Pittsburgh bed, which has a relatively large spore content in comparison with either the Redstone or the Sewickley beds, both of low spore content.

GENERAL CHARACTERS OF THE PITTSBURGH COAL.

As already intimated, the Pittsburgh bed begins at the bottom with an anthraxylous[a] coal, with little attritus intermixed (Plates V and VI.) In going upward, the relative amount of attritus increases and the amount of anthraxylon decreases gradually, so that at the top of the bed the conditions are exactly reversed. (Plates VII, VIII, and IX.) The bed is there very attritious, and contains relatively little compact anthraxylon. The lower part therefore contains but few spores, but their number increases with the increase in attritus until towards the top, and including the rooster coal, the coal is rich in spore matter. This is to be taken as general, as thin layers are found almost anywhere which are richer in both attritus and spore matter than in the average, or visa versa. Spores are found in the attritus only, never in the anthraxylon. The anthraxylous portions of the Pittsburgh coal are of a homogeneous, almost glassy appearance, of a light red color, and quite transparent as seen in thin section (Plate X *A*). In this respect the Pittsburgh coal is characteristic. Structures such as shown in Plate X *B* are also characteristic.

SPORES OF THE PITTSBURGH BED.

The spore content of the Pittsburgh bed is relatively high, and by far the largest amount of the spore matter is furnished by one kind of spore. So far, this spore has not been found in any other coal and shall be called in this paper the "Pittsburgh spore" (Plates XI *A* and *B*, XII *A* and *B*, XIII *A* and *B*, and XIV *A* and *B*). Besides this spore, another characteristic but much larger one—a small megaspore—is constantly found in the Pittsburgh bed, but in relatively small numbers (Plates XV and XVI *A* and *B*). We shall call this the "Pittsburgh megaspore."

Besides these two, three other spores, easily identifiable, are found—namely, (1) a large smooth, thick-walled megaspore, almost two millimeters (1 mm. = 1/25 inch) in diameter; (2) a smooth, thick-walled microspore; and (3) a large, thin-walled spore, besides several types of pollen grains found in fairly large numbers in some sections. But these play only a small part, and will not be considered further. For our purpose only the Pittsburgh spore and the Pittsburgh megaspore require further consideration, particularly the former, as it furnishes all the means required to establish the identity of the Pittsburgh coal.

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[a] See (1) A microscopic study of the Freeport coal bed, by Reinhardt Thiessen and A. W. Voorhees: Bull. 2, Carnegie Inst. of Technology, 1922, 75 pp.; and (2) Structure in Paleozoic Bituminous Coals, by Reinhardt Thiessen: Bull. 117, Bureau of Mines, 1920, 250 pp.

The Pittsburgh spore, the most characteristic spore of the bed, is relatively small but rather thick-walled. Seen in horizontal section it appears as a roughly circular to ovate disc, with an average diameter of 15 to 16 microns (1 micron = 1/25,000 inch. The surface is molded into closely-folded blunt serpentine ridges. (See Plates XIII *A* and *B* and XIV *A* and *B*.) These ridges are arranged symmetrically with respect to the tetrasporic markings consisting of long grooves across the discs, seen in Plate XIII *B*. It is only in relatively few spores where the grooves run over the face of the disc. In most cases this groove runs along the periphery of the disc. In all probability the groove formed the weakest line or the most flexible zone in the thick exine, and when put under pressure, and the spherical spore was compressed into the form of a disc, the bending occurred along this line, and hence came to lie along the periphery of the disc in most cases. In cross-section, the Pittsburgh spores present a somewhat irregular saw-toothed or crinkled appearance due to the serpentine ridges on the surfaces. (Plates XI *A* and *B* and XII *A* and *B*). In most sections these characters stand out clearly and sharply, and can be recognized at once, no matter from what part of the bed taken, except in the more highly metamorphosed Connellsville district, where the spores have suffered considerable change and have even partly or wholly disappeared.

The Pittsburgh megaspore is shown in horizontal section in Plate XV at 200 diameters, at 1000 diameters in Plate XVI *A*, and in cross-section in Plate XVI *B*. The surface is highly sculptured. The sculpturing consists of a complex system of rather irregular short ridges, irregular in orientation, better seen from the illustration than can be described. In cross-section the edges of the spore gives a fine, rather irregular, sawtoothed appearance, due to these irregular sculpturings on the surface (Plate XVI *B*).

SPORES IN THE REDSTONE BED.

The spore content of the Redstone coal is relatively low. In most sections relatively few spores are present (Plates XVII and XVIII); but here and there are sections in which the number of spores may be said to be large, as shown in Plate XXII *D*. But such sections are not numerous. As in the Pittsburgh bed, the bottom coal contains, as a whole, relatively few spores (Plates XVII and XVIII), but their number increases towards the top (Plate XX), reaching their maximum in the roof coal. As a whole, also, the spores are not nearly as well preserved as in the Pittsburgh bed. This is particularly true of the coal in the eastern part of the bed, where earth movements have had considerable effect on the nature of the coal.

The most characteristic and most prominent spore is that shown in Plates XVIII and XIX, and on account of its nature and structure will be called the "double-coated granulated spore." The size of this spore, as seen in cross-section, is quite variable, ranging from about 55 to 2000 microns. It must be remembered, however, that in measuring circular objects like spores, and in particular, spores of larger sizes in cross-sections, it can not be definitely known whether the section is at the diameter at a secant or even a tangent. Yet, taking this into consideration, it appears that the spore is variable in size. Its shape is rather peculiar and irregular, and it is often lenticular, tapering off to a fine edge, usually more or less folded upon itself, as shown in (Plate XIX *D*). The spore is composed of two layers—an outer and an inner. The former is of a light yellow color and very granular, and usually thicker than the inner layer; the inner layer is of a brownish-yellow color, and less granular. The granular nature of the spore is probably its most characteristic feature; and by means of it alone it can easily be distinguished, and even a small fragment may be easily recognized. On account of its irregular shape no definite form has been made out in horizontal sections. This spore is fairly uniformly distributed from the bottom to the top of the Redstone bed, but in relatively small numbers. It is also present in the Sewickley bed in similar form, but in smaller numbers. On account of its make-up and physical structure it will be called the "double-coated granular spore."

A second characteristic spore is that shown in Plates XXI and XXII, *A*, *B*, and *C*, a number of which are shown at a lower magnification in Plate XX. This spore is of a more regular shape and is thick-walled, of the size of a small megaspore, 70 to 90 microns in diameter. This spore is rarely found in the bottom coal, but towards the top, and in particular in the top coal, it is found in considerable numbers in some sections. A spore very similar to this one is also found in the Sewickley coal, in larger number, and is there fairly prominent. Because this spore is found in both the Redstone and Sewickley beds it will be called the "Redstone-Sewickley megaspore."

A third characteristic spore is that shown in Plates XXIII and XXIV *A, B, C*. This spore is somewhat larger than that described above, and its surface is profusely sculptured with short echinate spines whose bases form rough hexagons. At first sight it would seem that the sculpturing of this spore were the same as that of the Pittsburgh megaspore, but on closer examination is seen to differ markedly, in that the sculpturings of the Pittsburgh spore consists of more or less continuous irregular ridges, while in this spore it consists of short echinate spines with polygonal bases, as is shown in the illustrations. However, this spore is rarely met with.

Besides these three characteristic and well-defined spores, there are a number of smaller nondescript spores and pollen grains (Plate XXII*D*), without definite characters by means of which they could be identified easily. These also follow the general rule of distribution. They are few in number in the bottom coals, and increase in number towards the top, being numerous in some layers.

OTHER CHARACTERS OF THE REDSTONE COAL.

The bottom coal of the Redstone bed is anthraxylous—that is, the coal substance is derived largely from the woody parts of plants, and contains but little attritus (Plate XVII and XVIII). This condition changes towards the top, becoming less anthraxylous and more attritious, so that the top coal is more attritious than it is anthraxylous. Plate XX is from coal taken from near the top. The coal substance as a whole is of a much less dense consistence than the Pittsburgh coal, and is devoid of the glassy appearance common to the Pittsburgh coal. The physical structure of the Redstone coal is such that the ultra particles can be seen at a high magnification by means of ordinary illumination by stopping down the diaphragm.

The Redstone coal is fairly high in mineral matter. A large part of this consists of sericitic mica and kaolin which have probably been formed by the disintegration of feldspar, a considerable amount of which also is present.

SPORE MATTER IN THE SEWICKLEY BED.

The spore content in the Sewickley coal is, on the whole, still lower than that in the Redstone coal. As in the other beds, the lower part of the bed is very anthraxylous, and hence also contains relatively few spores (Plates XXV and XXVI). The anthraxylon decreases proportionately towards the roof, while the attritus increases until in the roof coal the proportion of attritus is greater than that of the anthraxylon. Plate XXVII is a section taken 36 inches above the floor. The amount of spore matter increases with the attritus, so that in the coal towards the roof it is much richer in spore matter than in the bottom coal. Plates XXV, XXVI, and XXVII are characteristic sections in order upwards. On the whole, the spores are rather poorly preserved, but enough of the characters of the characteristic spores have been preserved to make them fairly easily recognizable. The coal as a whole is highly laminated, being largely compiled of thin layers of anthraxylon and attritus (Plates XXV and XXVI). Much of the coal is coarsely granular in appearance and is resinous. The coal substance is of a loose physical structure, much like the Redstone coal in this respect.

The most characteristic spore in the Sewickley bed is a small crinkled one, shown in Plate XXVIII *A* and *B*, XXIX *A* and *B*, and XXXI *B* and *C*. It has been found in this bed only, and will be called the "Sewickley spore." It resembles the Pittsburgh spore fairly closely, both in its appearance in cross and in horizontal sections. On closer inspection, however, it is found to differ in several respects. Its size is somewhat larger than the Pittsburgh spore, measuring approximately between 18 and 20 microns by 20 to 25 microns, the disc being usually oval. The sculpturings consist of broad and blunt echinate spines or humps, and not of serpentine ridges as in the Pittsburgh spore. The sculpturings lend the spore a crinkled appearance similar to that in the Pittsburgh spore, but it is coarser, the crests being higher and the distances between the crests on the whole being greater than those in the Pittsburgh spore. The distinction in the differences in these two spores require, however, careful observation at a high magnification with good lenses. The large number of these spores in the Pittsburgh coal and the relatively small number in the Sewickley coal aids decidedly in distinguishing between them.

A second characteristic spore is shown in Plate XXXI, *D* and *E*. It is conspicuous and easily recognizable. It has rather thick walls, either smooth or with a few elevations, as shown. As seen in cross-section, the spore is from 600 to 700 microns long and 50 to 100 microns thick. This type of spore also occurs in the Redstone coal in larger numbers, particularly towards the top of the bed. Its sculpturing in the Sewickley coal is probably slightly different, but not enough to make a distinction easily. Because it is found in both of these coals it will be called the "Redstone-Sewickley megaspore."

A third characteristic spore found throughout the Sewickley bed is the double-coated granular spore, shown in Plate XXXII *A*, *B*, *C*, *D*, and already described under the spores of the Redstone coal. This spore is, however, not nearly as prominent nor nearly as numerous, and not as well preserved as in the Redstone coal.

A fourth characteristic spore is that shown in Plates XXX *A* and *B*, and XXXI *A*. This spore is also found in the Redstone coal, but is here found in still smaller numbers than in the Redstone coal; in fact, it is rarely met with. In cross-section it could not be distinguished from that in the Redstone coal, and in horizontal section the sculpturings appear to be coarser. Its size, on the whole, is probably the same as in that of the Redstone coal, although that shown is somewhat larger.

In addition to these four characteristic spores, a number of other spores—both microspores and megaspores—and pollen grains are present in considerable numbers in some layers. These show no characteristic markings, and being mostly poorly defined are classed as nondescript.

IDENTIFICATION OF THE COALS BY THE SPORES STUDIED AS CRITERIA.

1. A coal from the Pittsburgh bed may readily be recognized primarily through the Pittsburgh spore, but also by the characteristic appearance of the coal itself, and the large number of spores as a whole.

2. The Redstone coal may be distinguished (1) by the presence of the double-coated granulated spore; (2) by the absence of the Pittsburgh spore; (3) by the absence of the Sewickley spore; and (4) by the presence of the Redstone-Sewickley megaspore. The two spores to be identified, therefore, are the double-coated granulated and the Redstone-Sewickley spores from among a number of nondescript spores. The most characteristic one is the double-coated granulated spore, its numbers increasing from the bottom towards the roof. The Redstone-Sewickley megaspore is, however, constantly present in smaller numbers.

The general appearance of the coal—that is, the dark red color, the coarse colloidal condition, the resinous nature of the anthraxylon and the relatively small number of the spores—must be taken into consideration and serve as criteria.

3. The Sewickley coal should be recognized by the Sewickley microspore, through its crinkled appearance in cross-section and the coarse blunt echinate spines with approximate hexagonal bases. The small number as a whole, and the coarse, blunt, echinate sculpturing should distinguish this spore from the Pittsburgh microspore found in the Pittsburgh bed in larger numbers, smaller in size, and with serpentine sculpturing.

The Redstone-Sewickley megaspore and the double-coated granulated spore, the former in larger numbers than the latter, should be present. The finely striated condition and the heterogeneous appearance and the resinous condition of the coal are also characteristics which must be taken into consideration.

4. In all of the coals it was found that the characters are best preserved in the coals taken from the region of the bed about one-third the distance of its thickness from the floor to within one-third of its thickness from the roof. The roof coal, however, always contains better preserved material than the floor coal; the poorest preserved characters were always found in the floor coal. In thin beds the characters are less well-preserved than in thick beds.

5. In more highly metamorphosed regions of a bed, as for example in the beds towards Chestnut Ridge and Laurel Ridge, Pa., where the coal has been subjected to a considerable earth thrust, the characters are less well-preserved than in regions farther away from it; and as the axis of this uplift is approached the coals become more difficult to work with. As a rule, coals high in volatile matter and low in fixed carbon are best for examination. With the increase of fixed carbon the coal becomes more opaque, and the spore matter takes on more the color of the humic matter and the anthaxylon, so that it becomes fairly difficult to distinguish it from these. Also, the spore matter appears to have more or less vanished in the regions in which the coal has been subjected to earth thrusts. Some of the spores have disappeared altogether, while others have partly disappeared. For this reason some samples of the Pittsburgh coal from the Connellsville region contained but little spore matter.

Also, in coals with a shallow cover, the characters, on the whole, are less preserved than in coals with a heavy cover. The same is true of coals exposed in an outcrop close to the surface.

SUMMARY AND CONCLUSIONS.

The Pittsburgh, Sewickley, and Redstone beds and coals of the Monongahela formation have been described; the correlation characters in the coals were studied; and the means whereby the coals may be identified are given.

The practical results of this investigation may be stated as follows:

1. The Pittsburgh coal can be identified easily by means of its characteristic spores and plant structure, even should only a small piece of coal be at hand, provided that it is not taken from the bed immediately above the floor.

2. The Redstone and the Sewickley coals can also be identified by a similar means. While they are easily distinguishable from the Pittsburgh coal, more care has to be exercised to distinguish them from one another.

3. Coals from regions where they have been highly metamorphosed or crushed through earth movements are not easily identified by this means, due to their opaqueness, alteration, and disappearance of characteristic constituents.

PLATES.

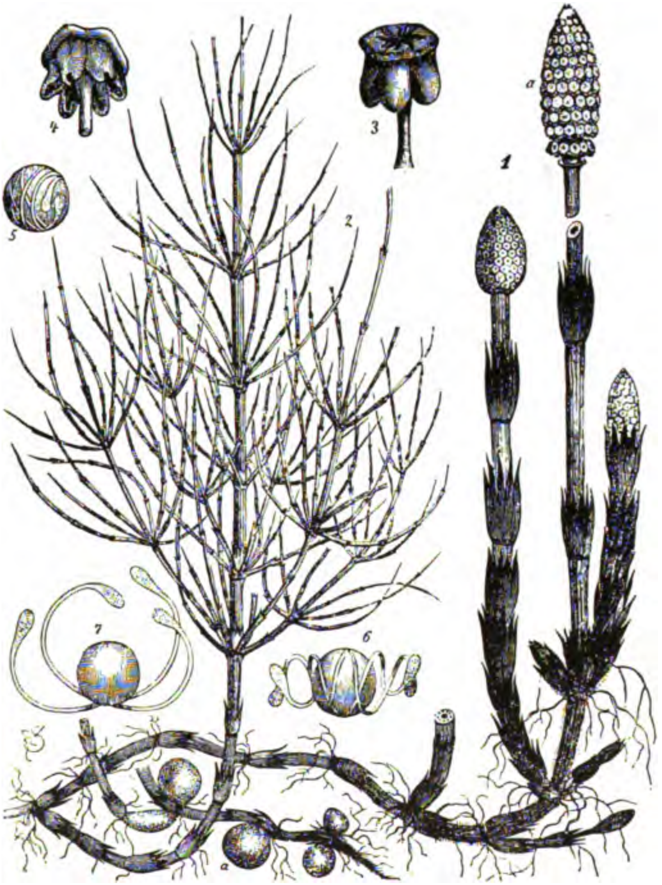


Plate I.—Equisetum arvense *or common horsetail, showing spores.*
(See pages 15 and 16.)

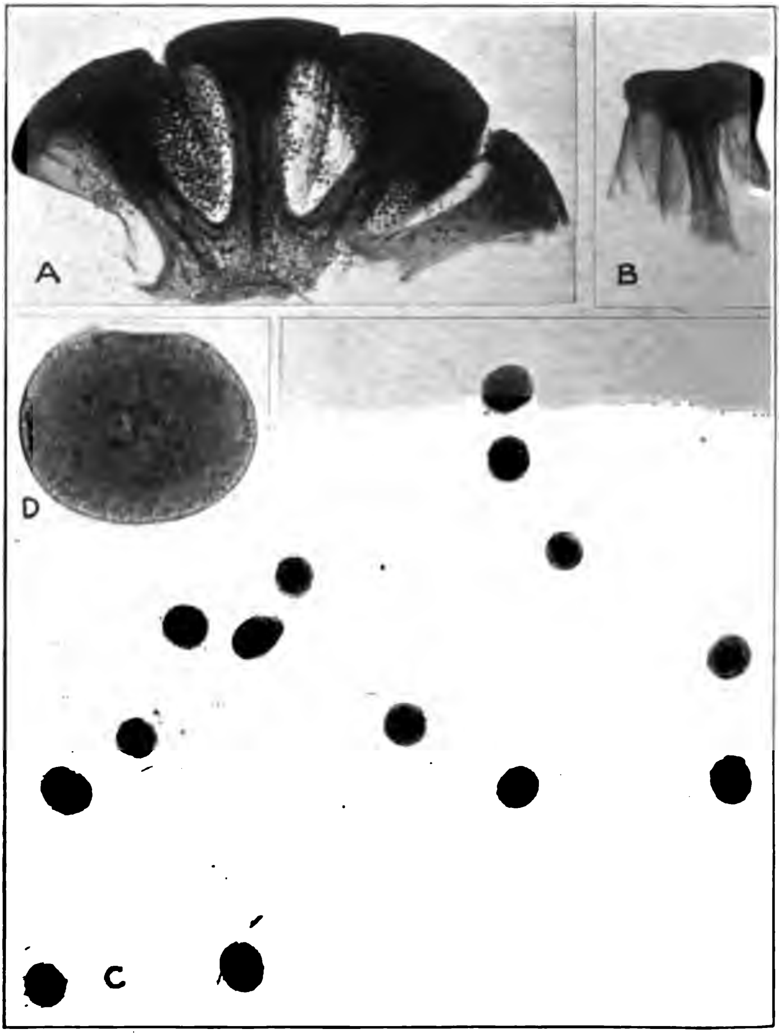


Plate II.—*Details of Equisetum arvense.* (See page 16.)

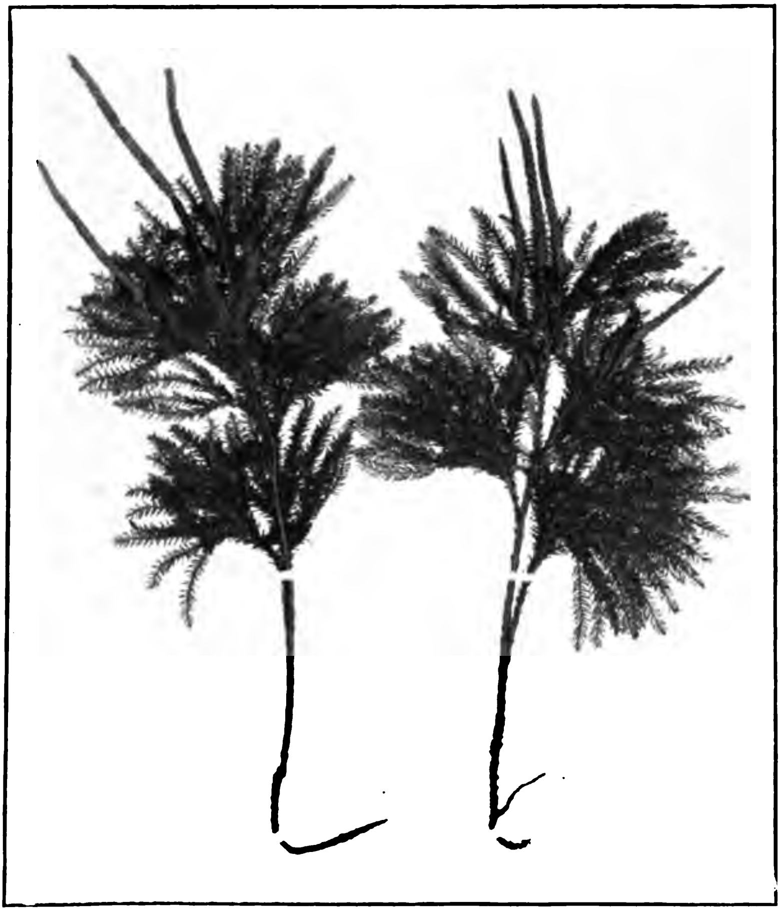


PLATE III.—*Two herbarum specimens of* Lycopodium obscurum, *a common ground pine or club moss, with cones.*

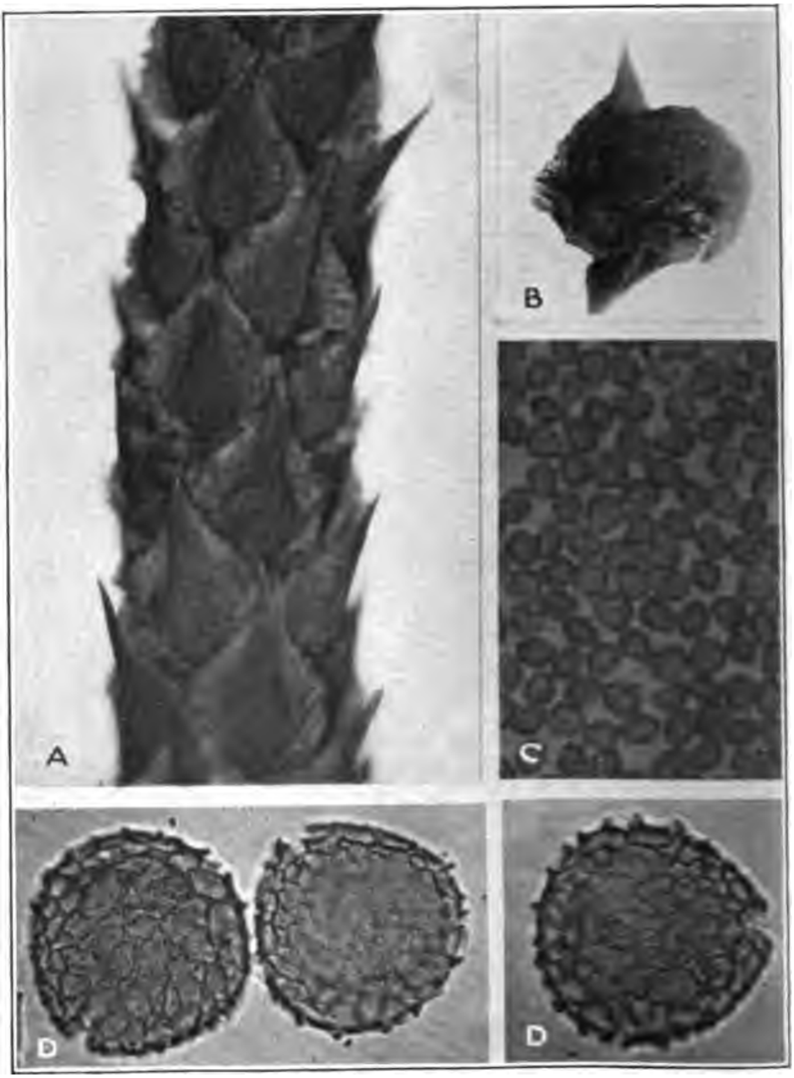


PLATE IV.—*Part of cone, etc., shown in Plate III.*

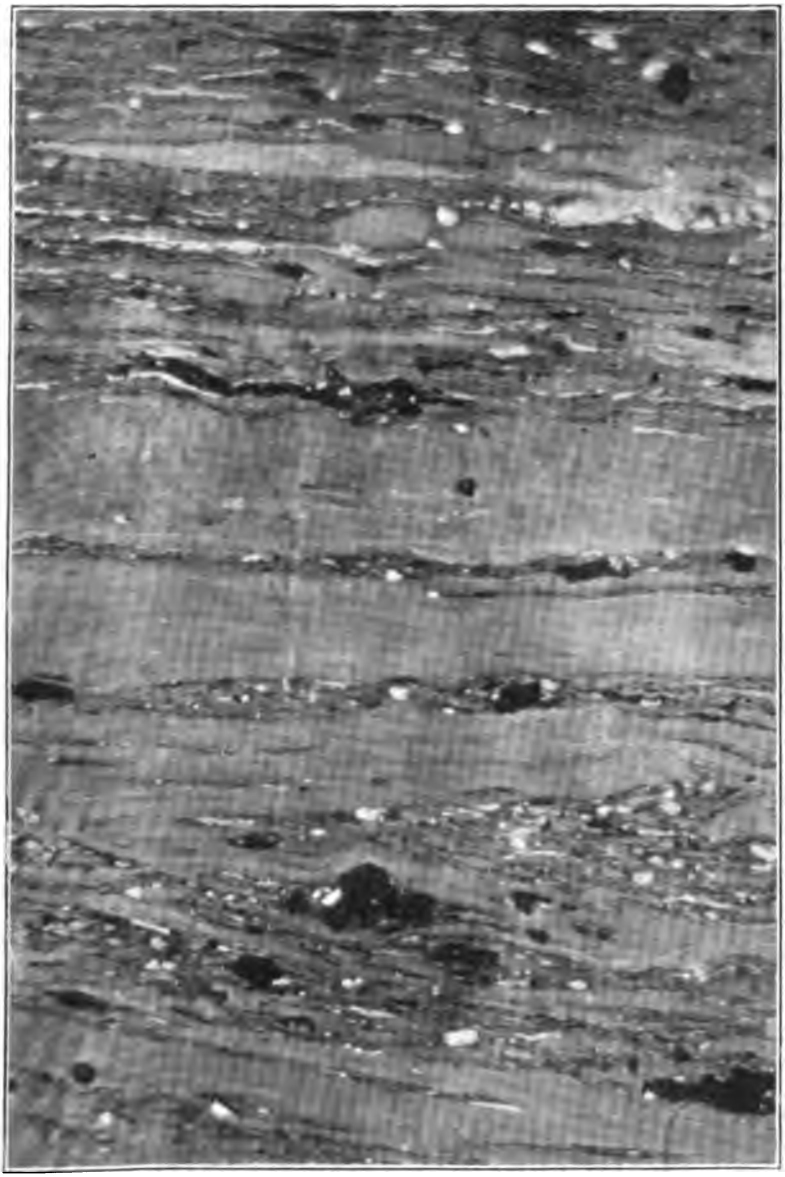


Plate V.—*Section of Pittsburgh coal from Experimental Mine, Bruceton, Pa., 4 inches above floor.*

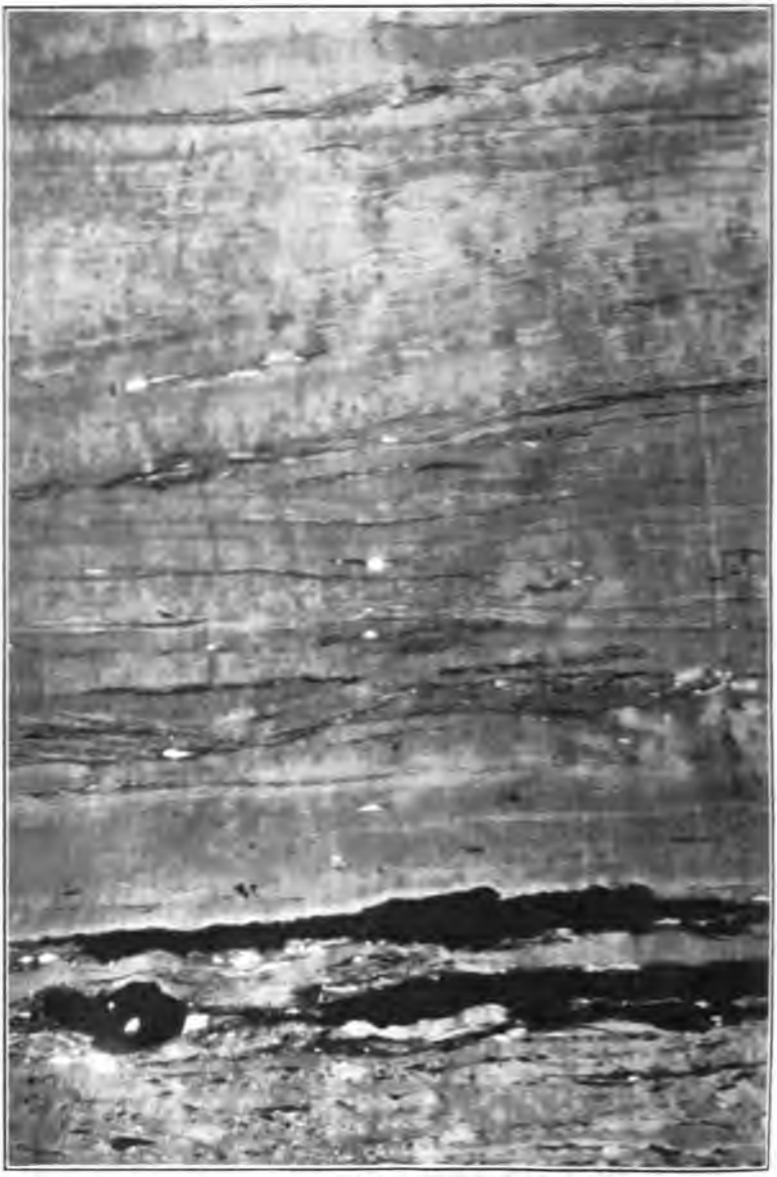


PLATE VI.—*Thin cross-section of Pittsburgh coal from Randall mine, Randall, W. Va., 12 inches above floor.*

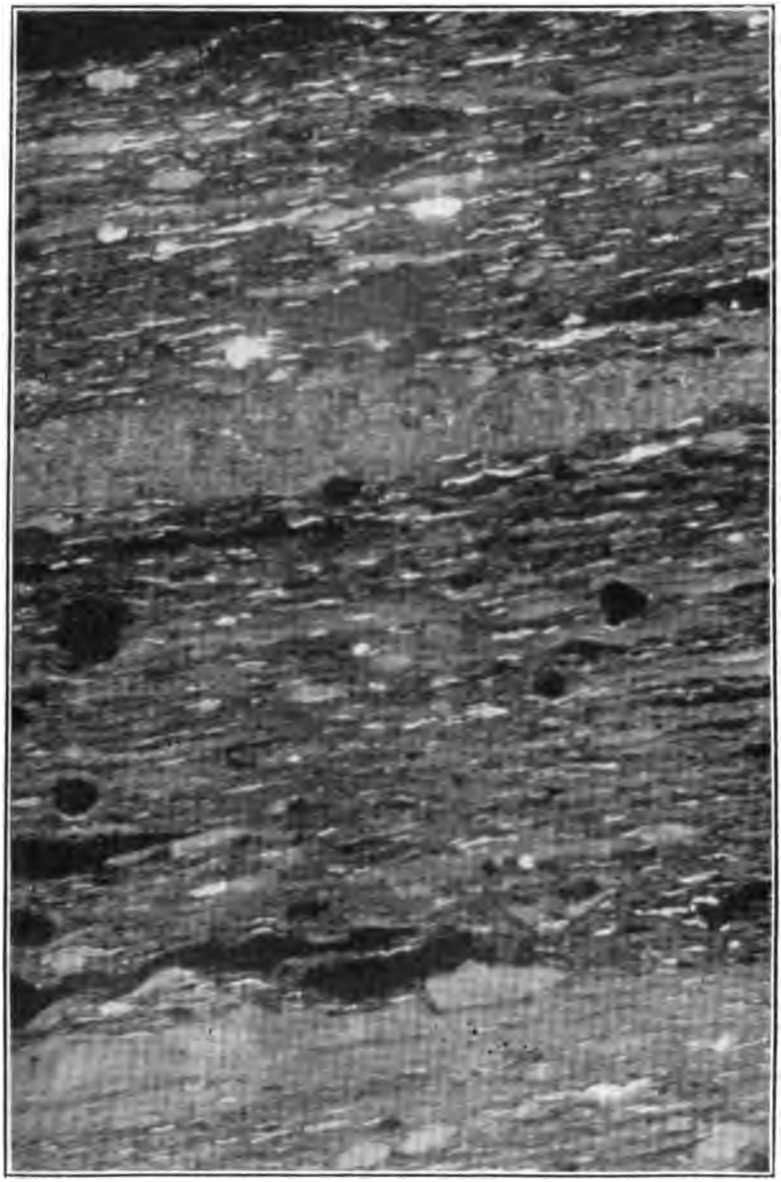


PLATE VII.—*Thin cross-section of Pittsburgh coal from Experimental Mine, Bruceton, Pa., 38 inches above floor, representing an attritious coal.*

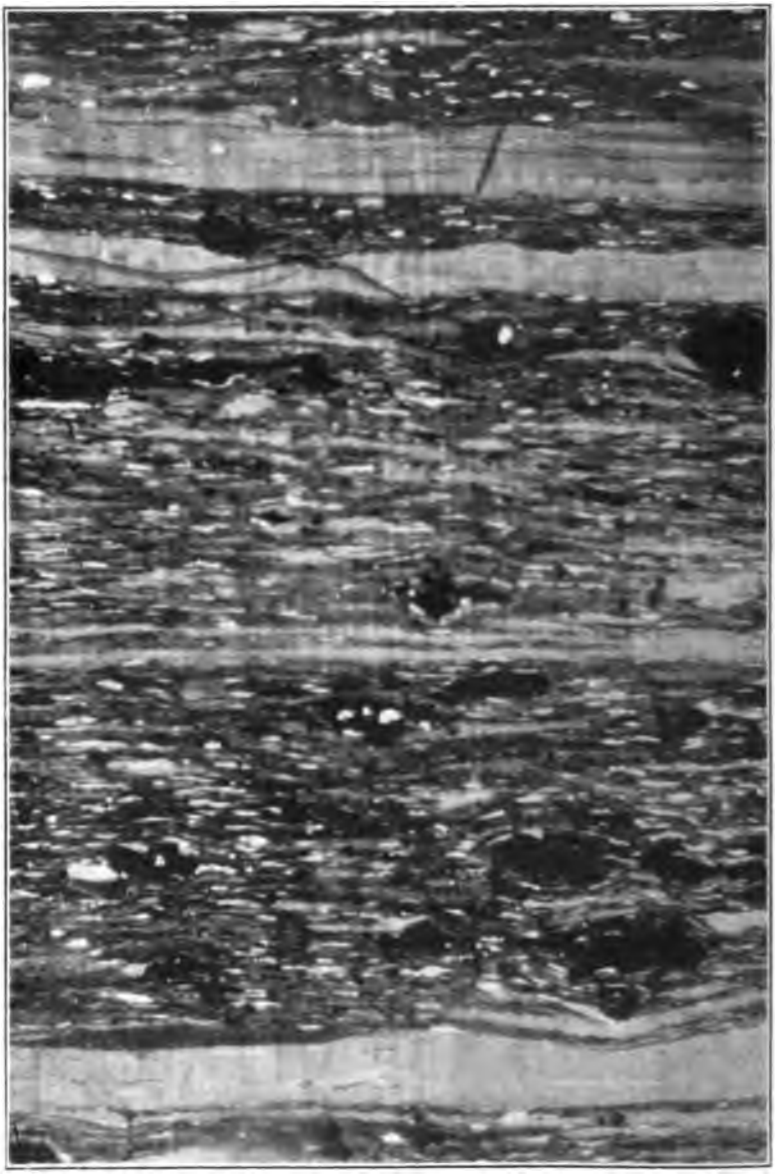


Plate VIII.—*Thin cross-section of Pittsburgh coal from Experimental Mine, Bruceton, Pa., from near top of bed. A typical attritious coal with large number of Pittsburgh spores.*

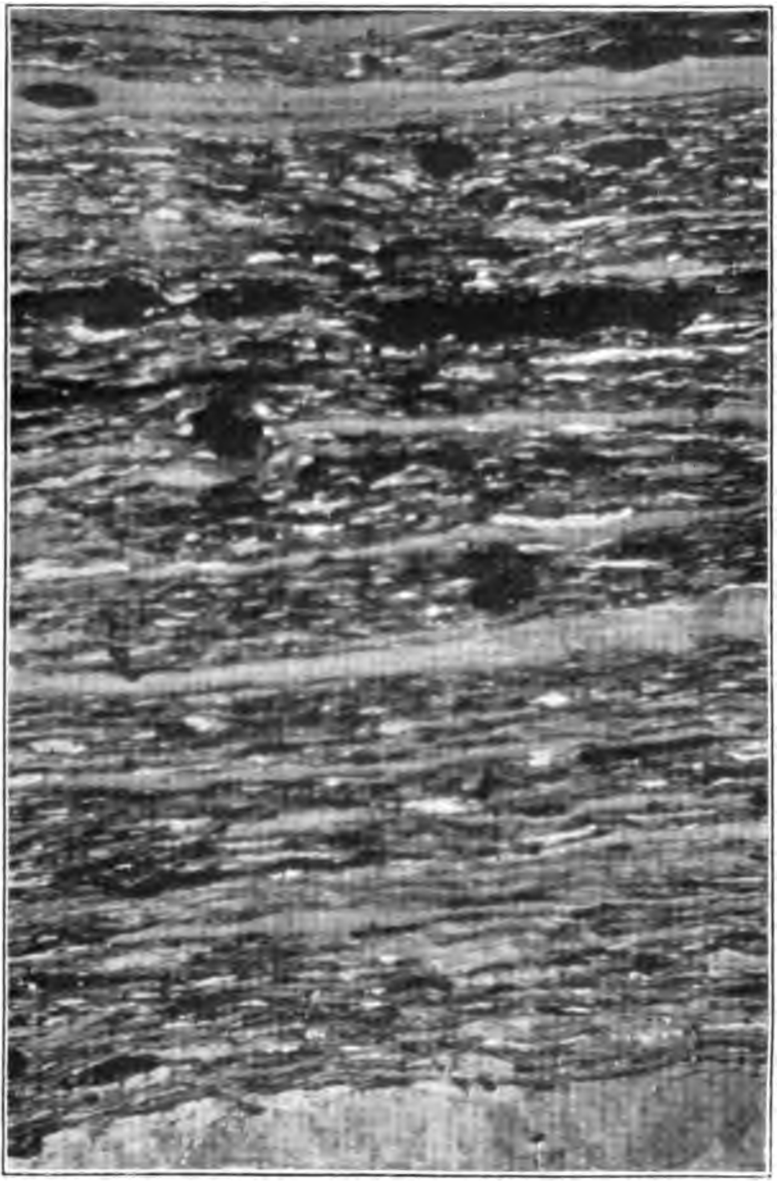


PLATE IX.—*Thin cross-section from Pittsburgh bed at Burgettstown, Pa., from near roof. A typical attritus.*

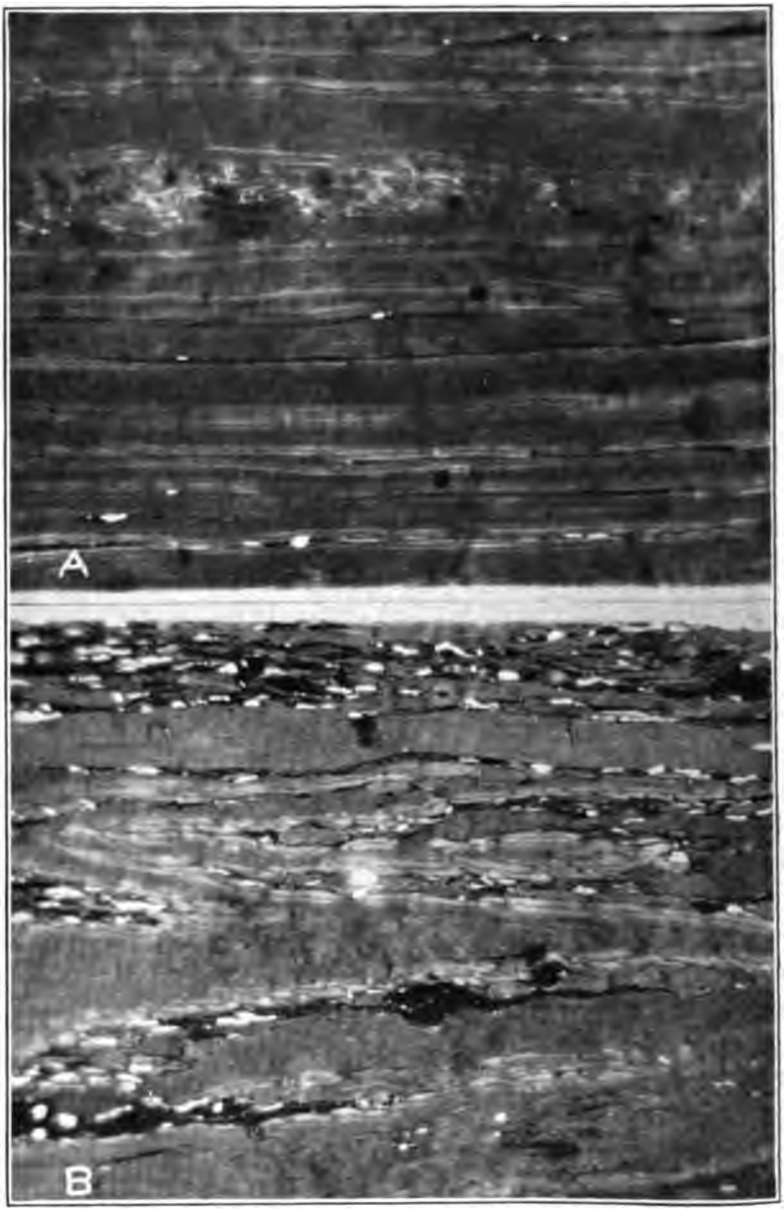


PLATE X.—A and B, *Section of Pittsburgh coal from Betty mine, Madison, Pa., showing a typical anthraxylous coal with but very little attritus, and but few spores.*

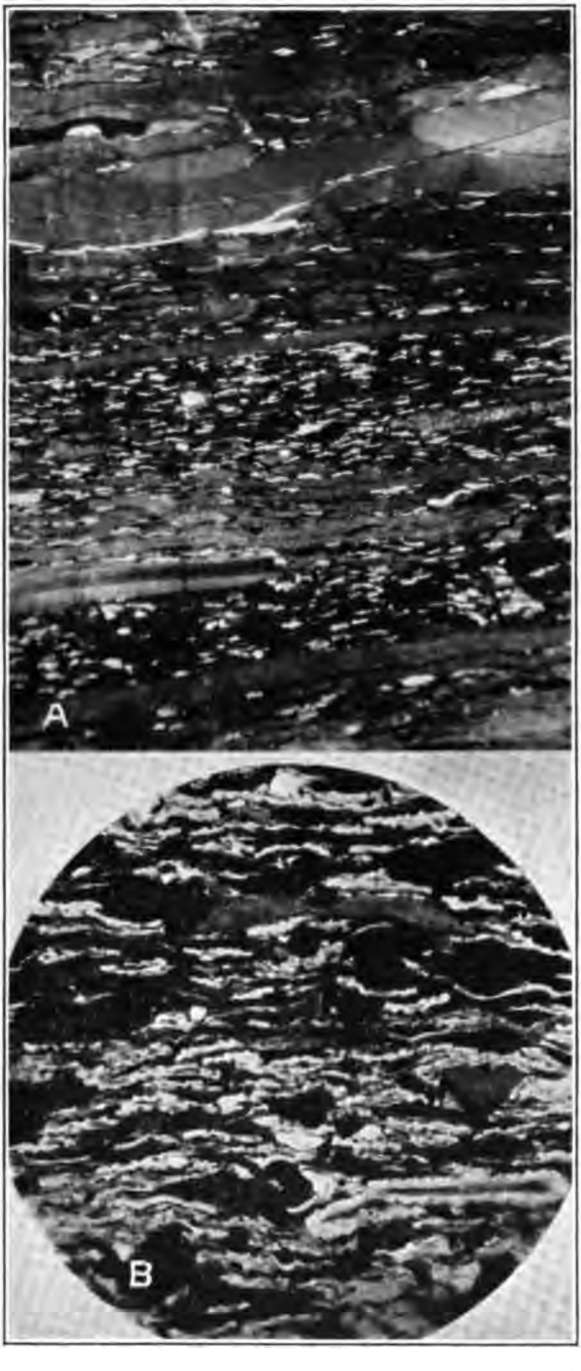


Plate XI.—A, *Thin cross-section of Pittsburgh coal from Experimental Mine, Bruceton, Pa. Attritus with thin strips of anthraxylon showing Pittsburgh spores.*

B, *Thin cross-section of Pittsburgh coal. Attritus showing appearance of Pittsburgh spore in cross-section at higher magnification than A.*

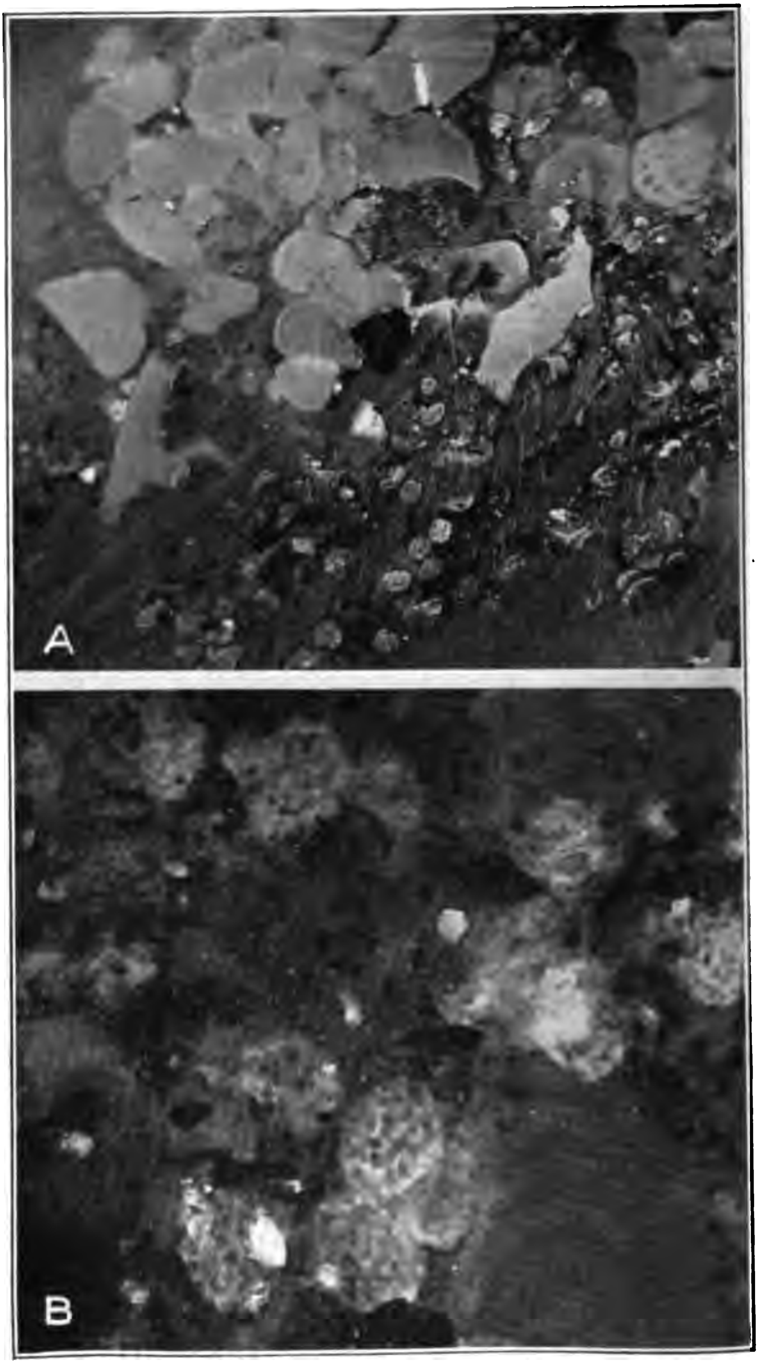


Plate XII.—A, *Thin cross-section of Pittsburgh coal from Experimental Mine, Bruceton, Pa. Typical section of attritus with Pittsburgh spore.*
B, *Part of section shown in A, more highly magnified, showing characteristic appearance of spore in cross section.*

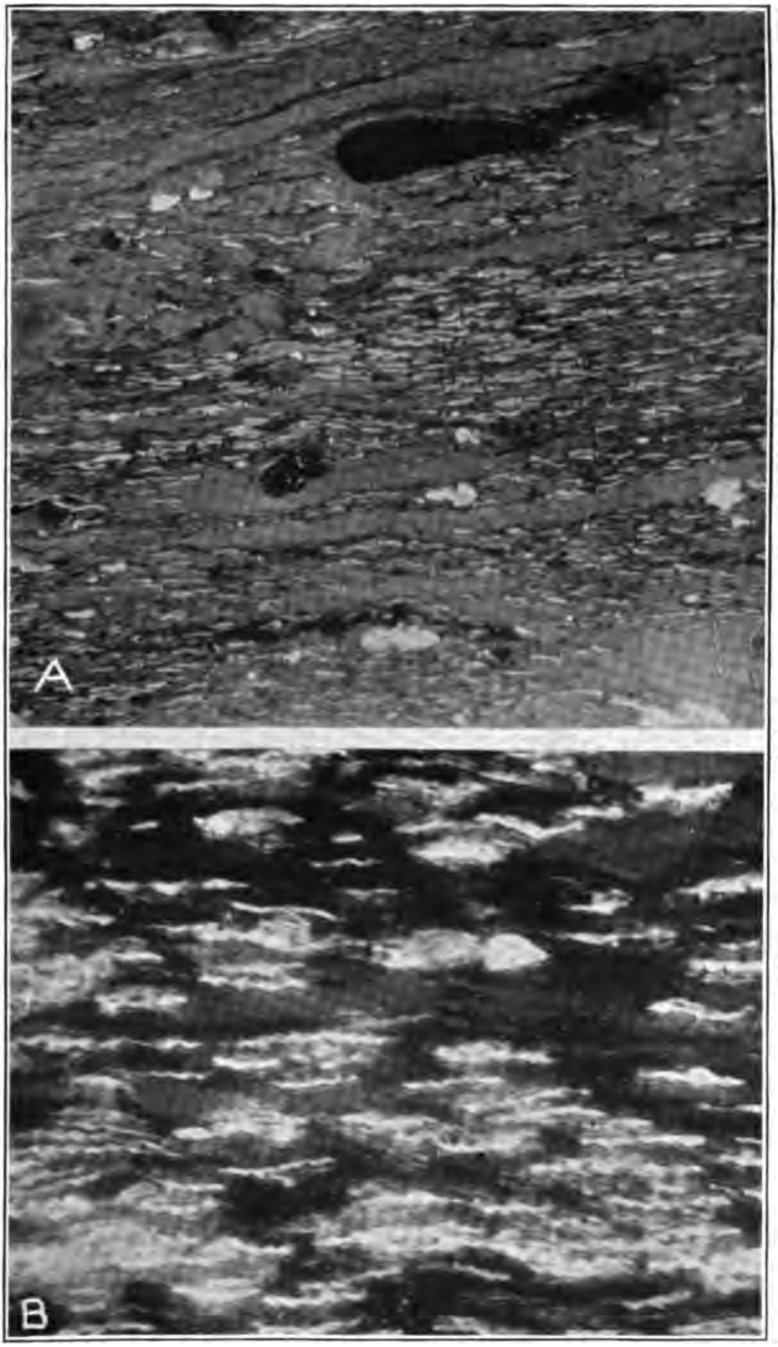


PLATE XIII.—A, *Horizontal section of attritus in Pittsburgh coal including a number of Pittsburgh spores.*

B, *Part of A, more highly magnified, showing sculpturings and Pittsburgh spores in detail.*

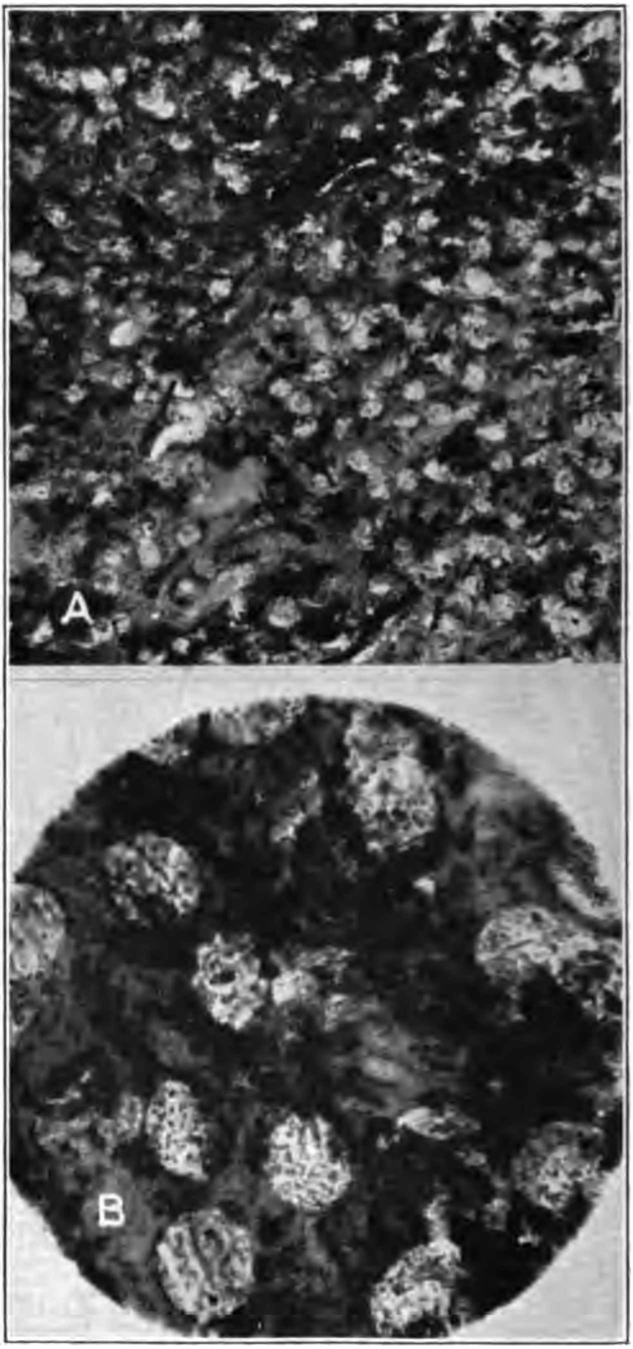


PLATE XIV.—A, *Horizontal section of Pittsburgh coal, including a number of resinous particles and some spores.*
B, *Part of A, more highly magnified, showing characteristic sculpturing of Pittsburgh spores in detail.*

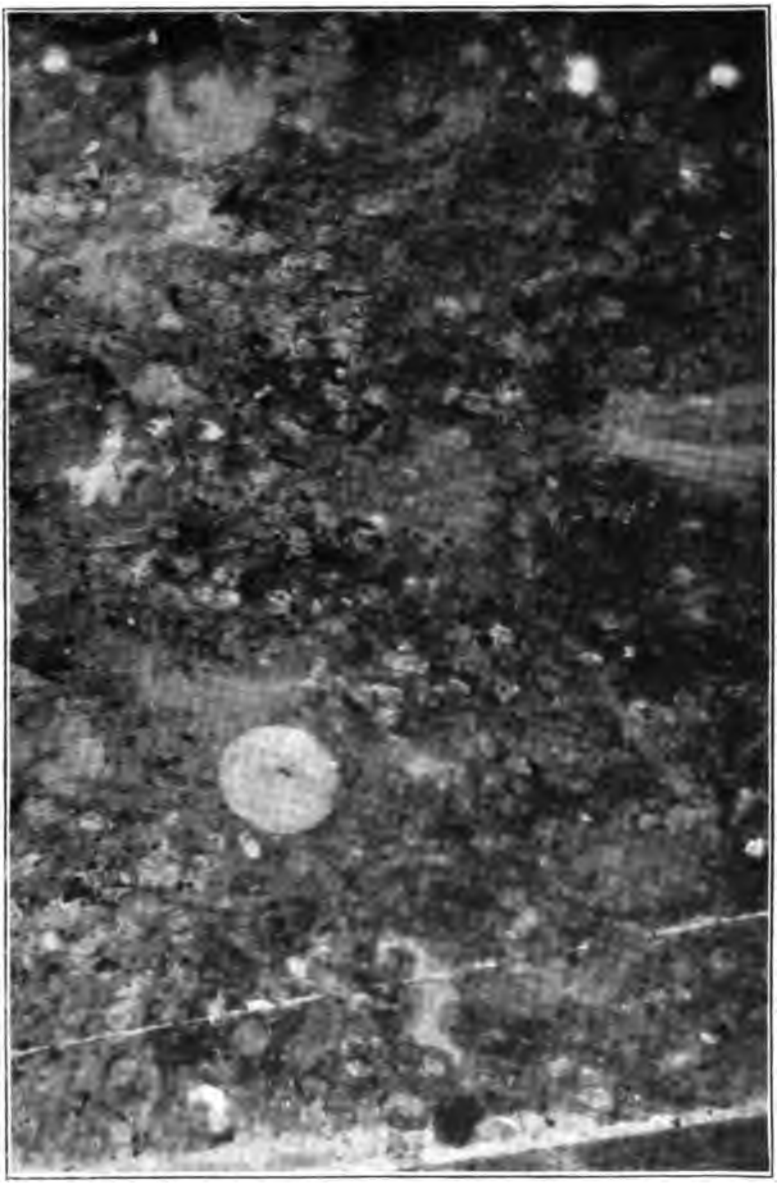


Plate XV.—*Horizontal thin section of Pittsburgh coal. Attritus with large number of Pittsburgh spores and a Pittsburgh megaspore, showing relative sizes.*

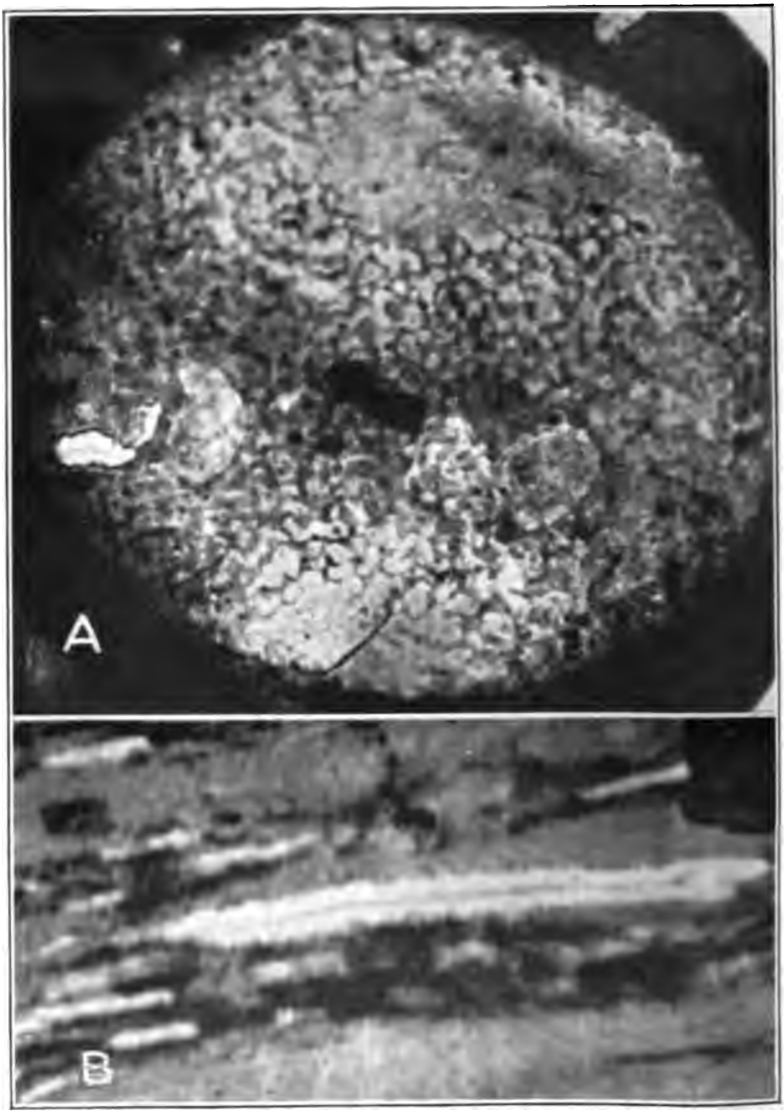


PLATE XVI.—A, *Horizontal section of Pittsburgh coal, part of Plate XV, including Pittsburgh megaspore more highly magnified, showing the sculpturing of this megaspore in detail.*

B, *Thin cross-section of Pittsburgh coal, including a Pittsburgh megaspore, showing the appearance of this spore in cross-section, and the relative size of the two Pittsburgh spores.*

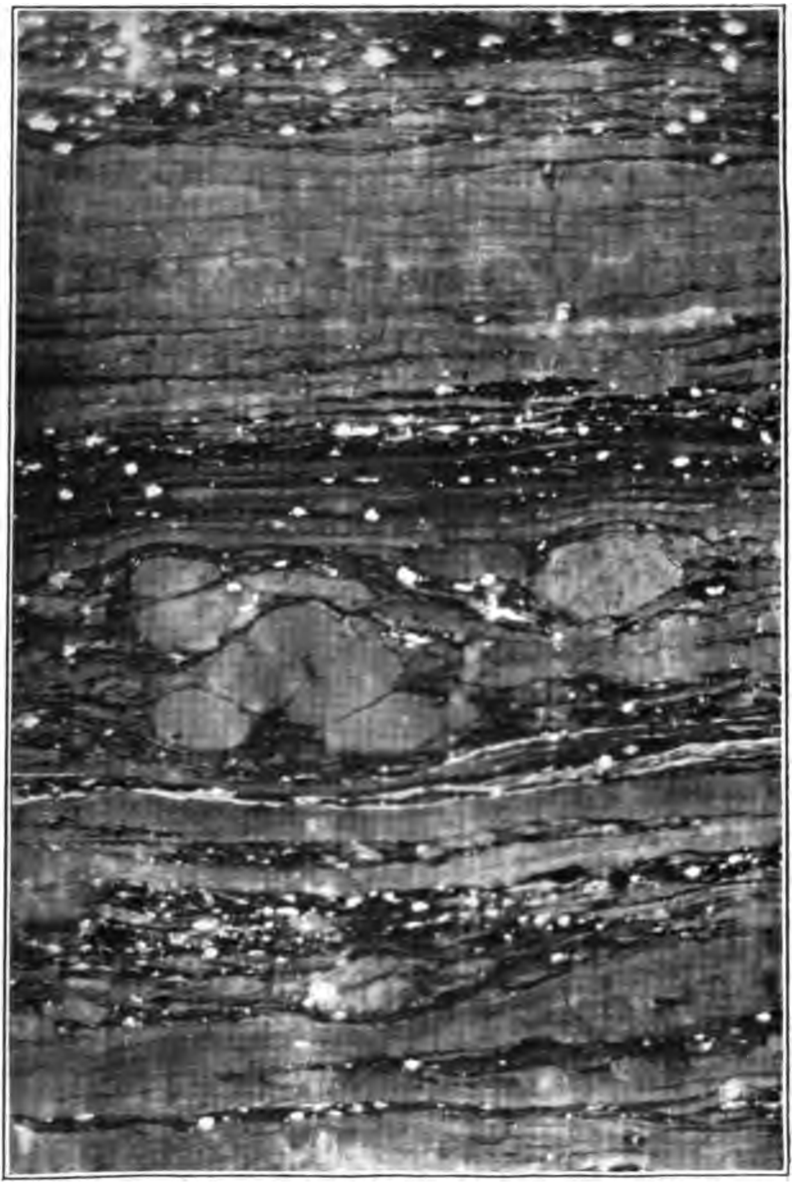


Plate XVII.—*Thin cross-section of Redstone coal from Betty mine, Madison, Pa., giving a general appearance of the coal in cross-section. Only a few nondescript spores are shown.*

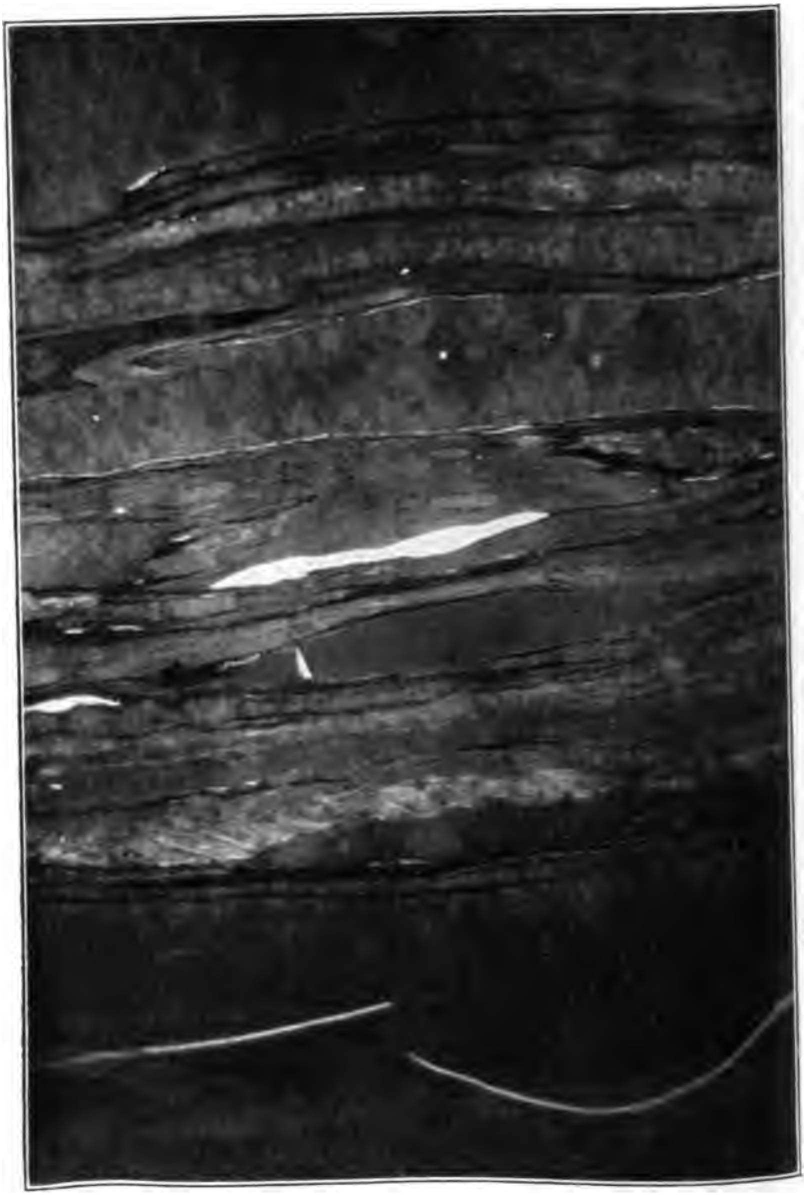


PLATE XVIII.—*Thin cross-section of Redstone coal from Pomeroy, Ohio, giving the general appearance of the coal in thin cross-section, including a double-coated granulated spore.*

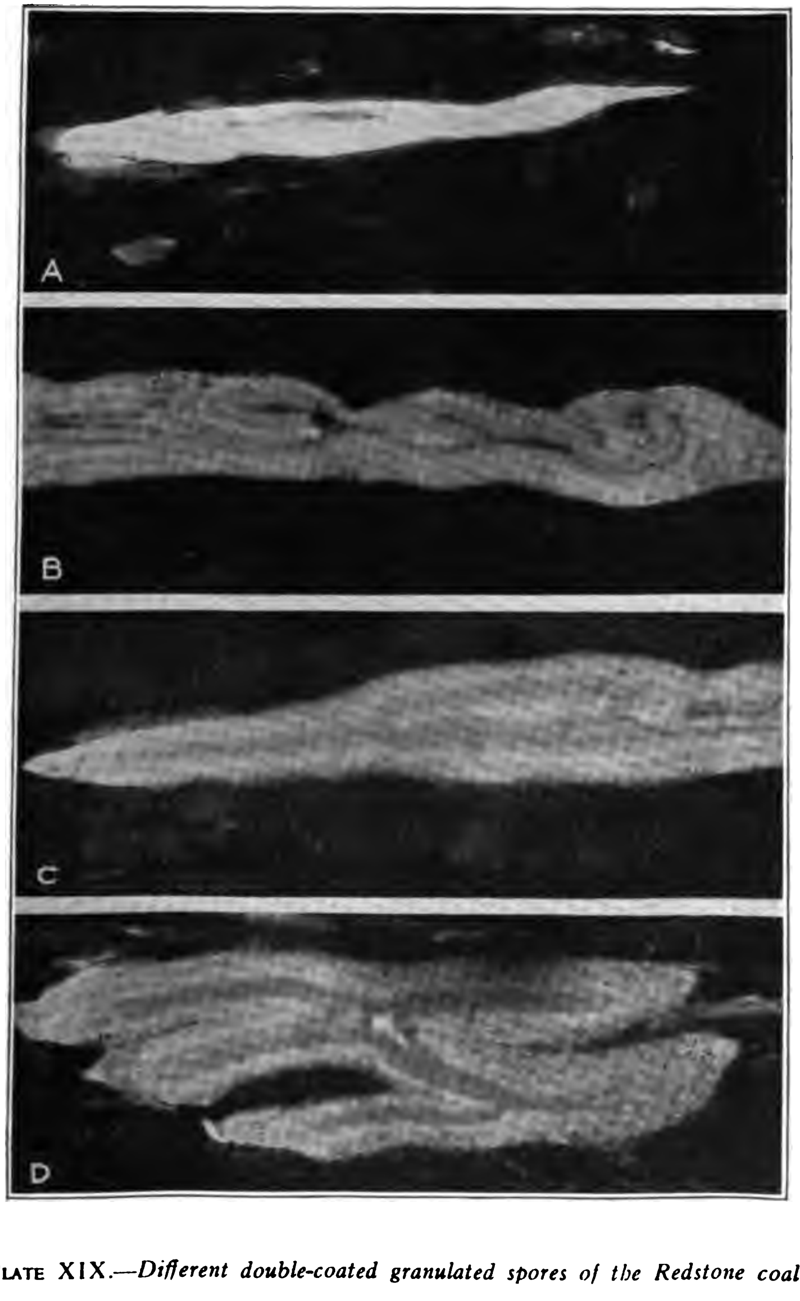


Plate XIX.—*Different double-coated granulated spores of the Redstone coal.*

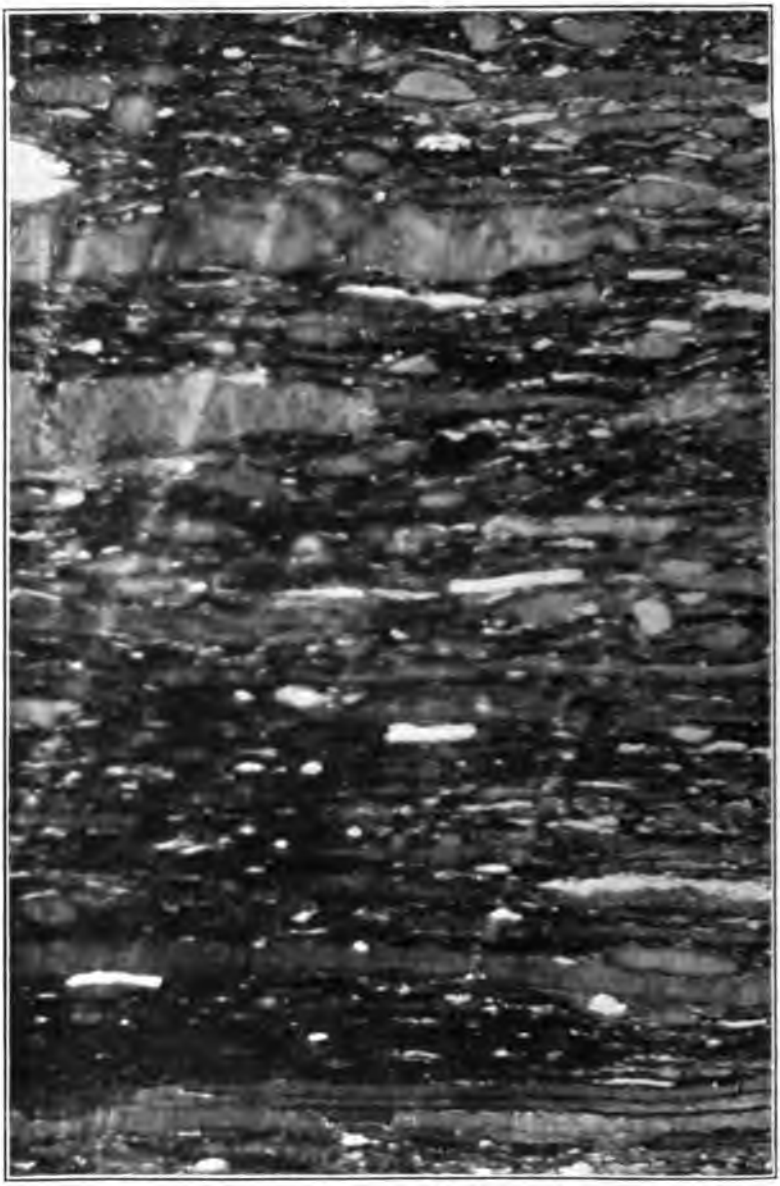


Plate XX.—*Thin cross-section of Redstone coal from Pomeroy, Ohio, showing general nature of the coal, and including a number of characteristic spores, and at higher magnification than Plate XXIV* A *and* B *and XXVI* C.

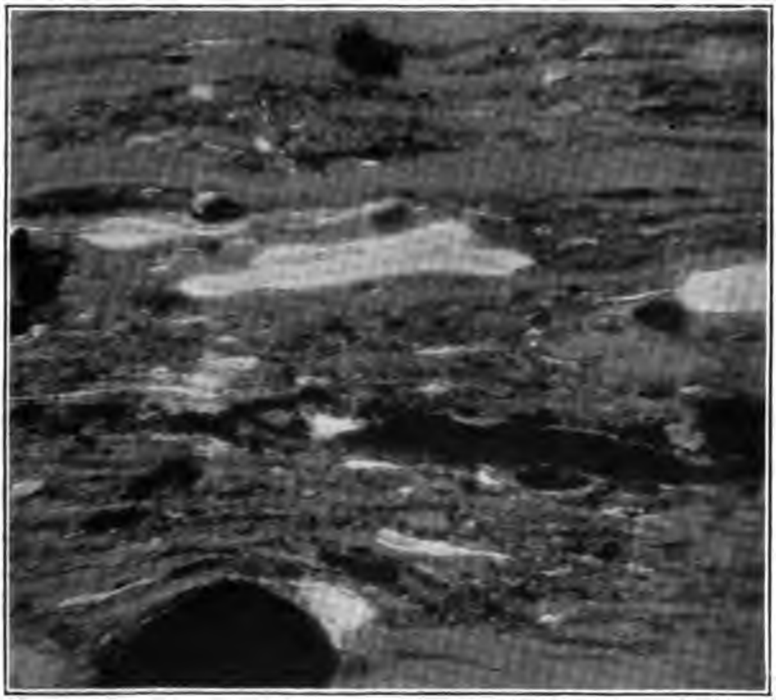


Plate XXI.—*Thin cross-section of Redstone coal from Pomeroy, Ohio, including a Redstone-Sewickley spore.*

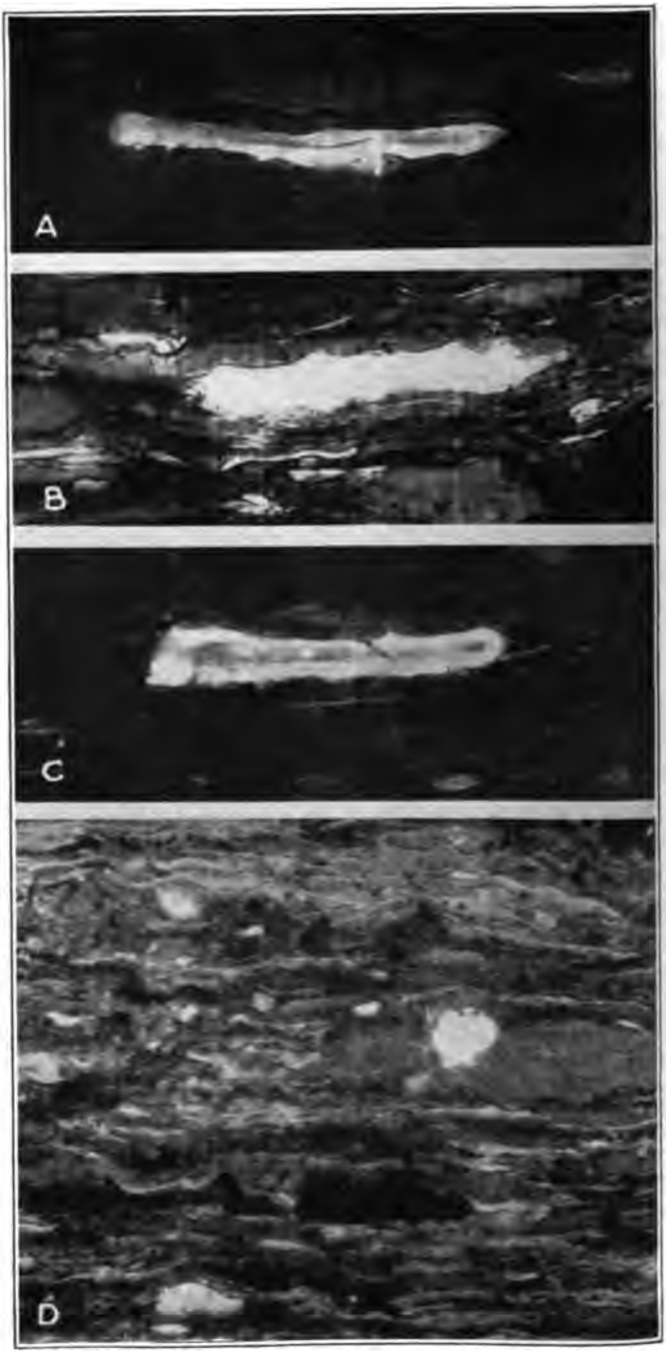


Plate XXII.—A, B, C, *Cross-section of Redstone-Sewickley spores of the section shown in Plate XX.*
D, *Thin cross-section of attritus of Redstone coal, including a large number of nondescript spores and pollen grains.*

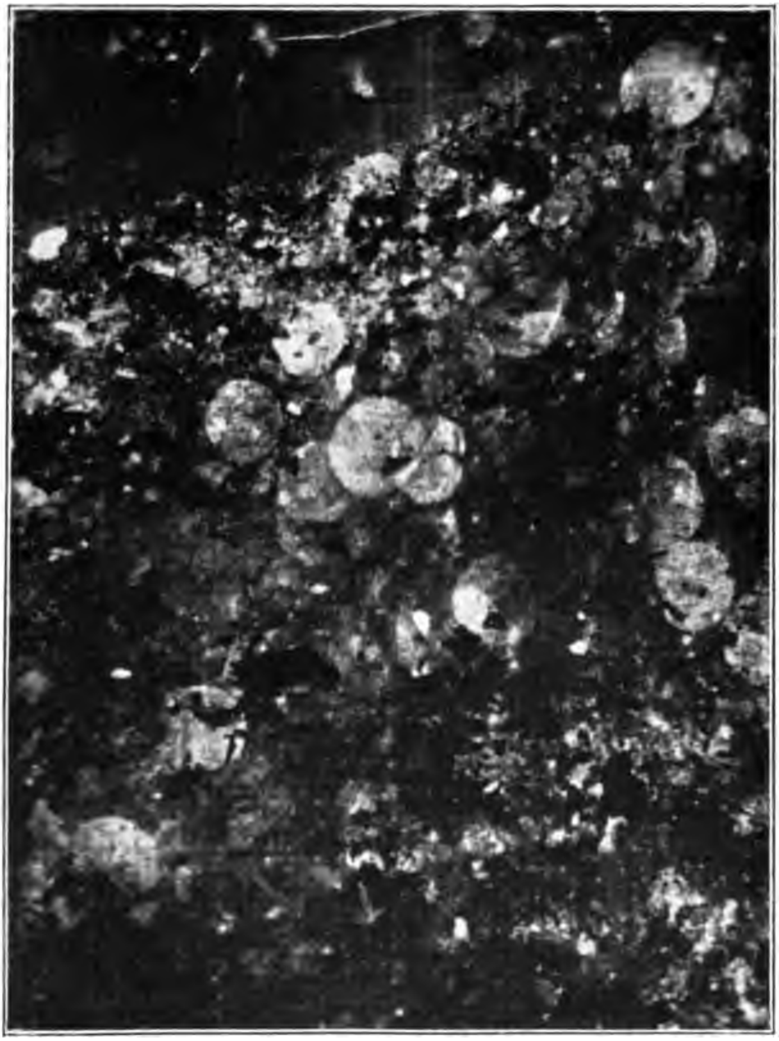


Plate XXIII.—*Thin horizontal section of attritus of Redstone coal from Pomeroy, Ohio, including a number of large spores, shown at a higher magnification than in Plate XXIV.*

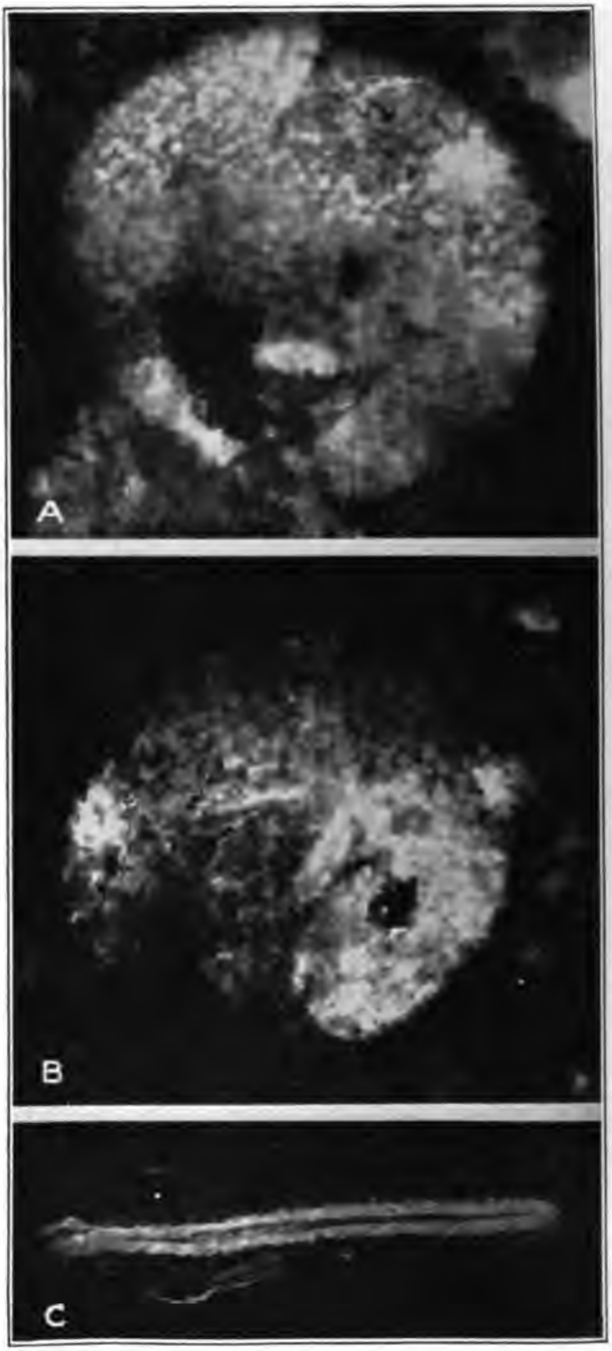


Plate XXIV.—A, *One of the spores shown in Plate XXII, at a higher magnification, showing the echinate sculpturing in detail.*
B, *The same spore as* A *at slightly different focus to show the polygonal bases of the echinate sculpturing.*
C, *The same spore as* A *in cross-section.*

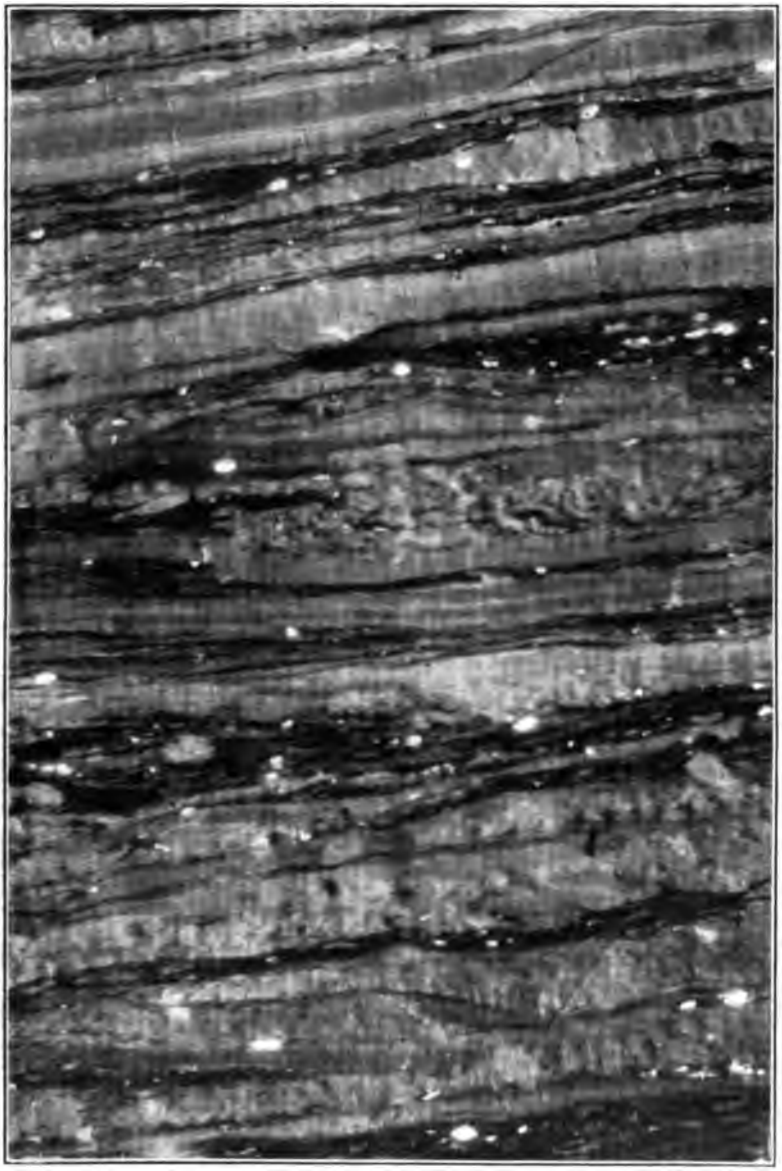


Plate XXV.—*Thin cross-section of Sewickley coal from Newcomerstown, Pa., showing the general nature of this coal in section.*

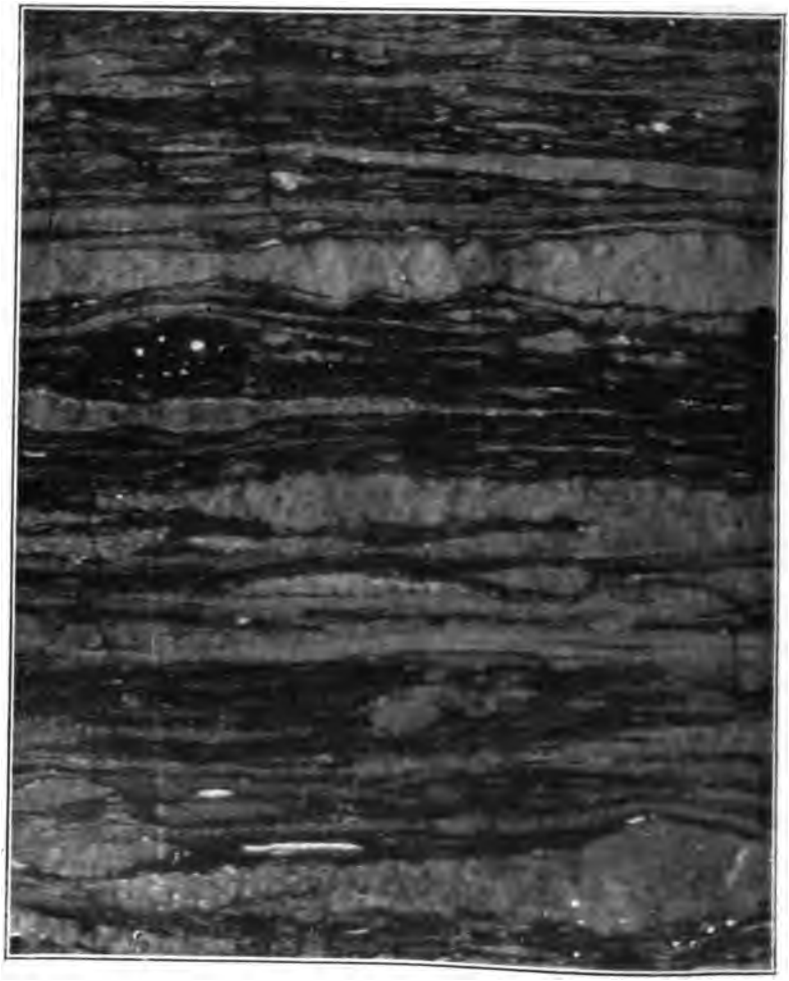


PLATE XXVI.—*Thin cross-section of Sewickley coal from the Belmont mine, Flushing, Ohio, showing general appearance of this coal in section.*

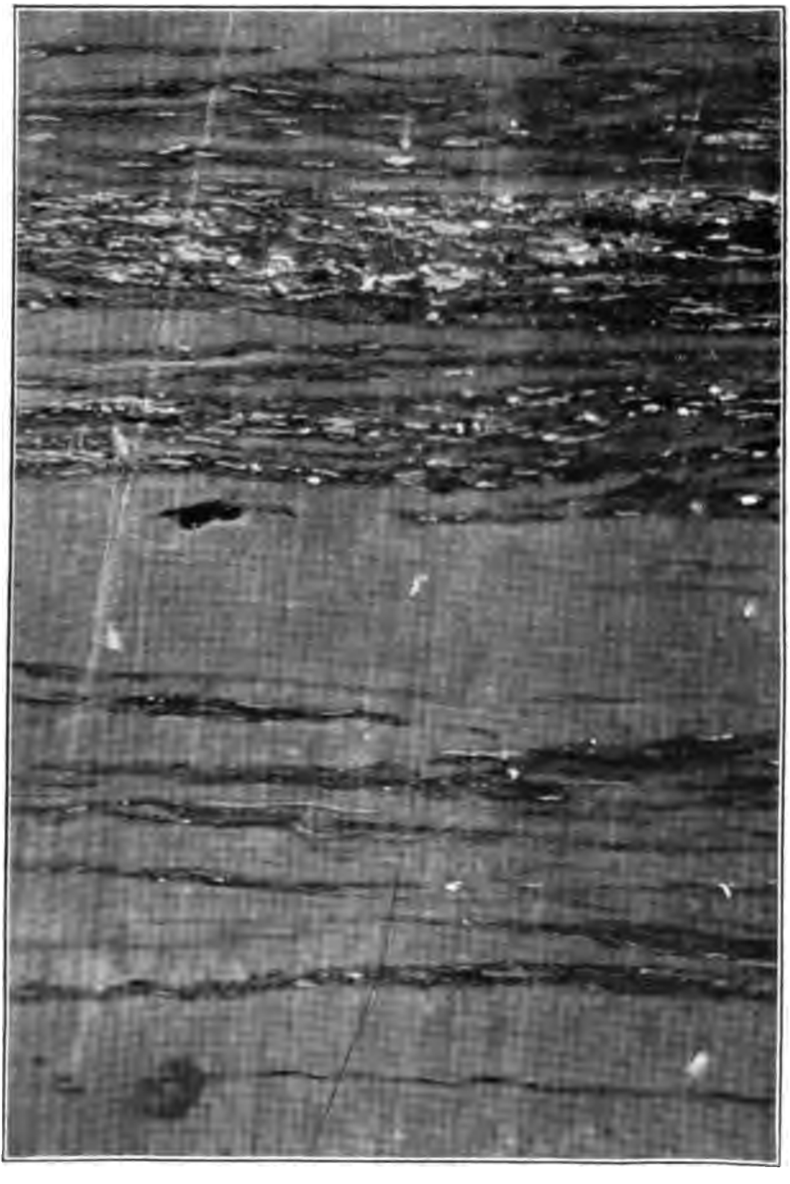


Plate XXVII.—*Thin cross-section of Sewickley coal from the Jarvis mine, Randall, W. Va., 36 inches above floor, showing general appearance of the coal in section.*

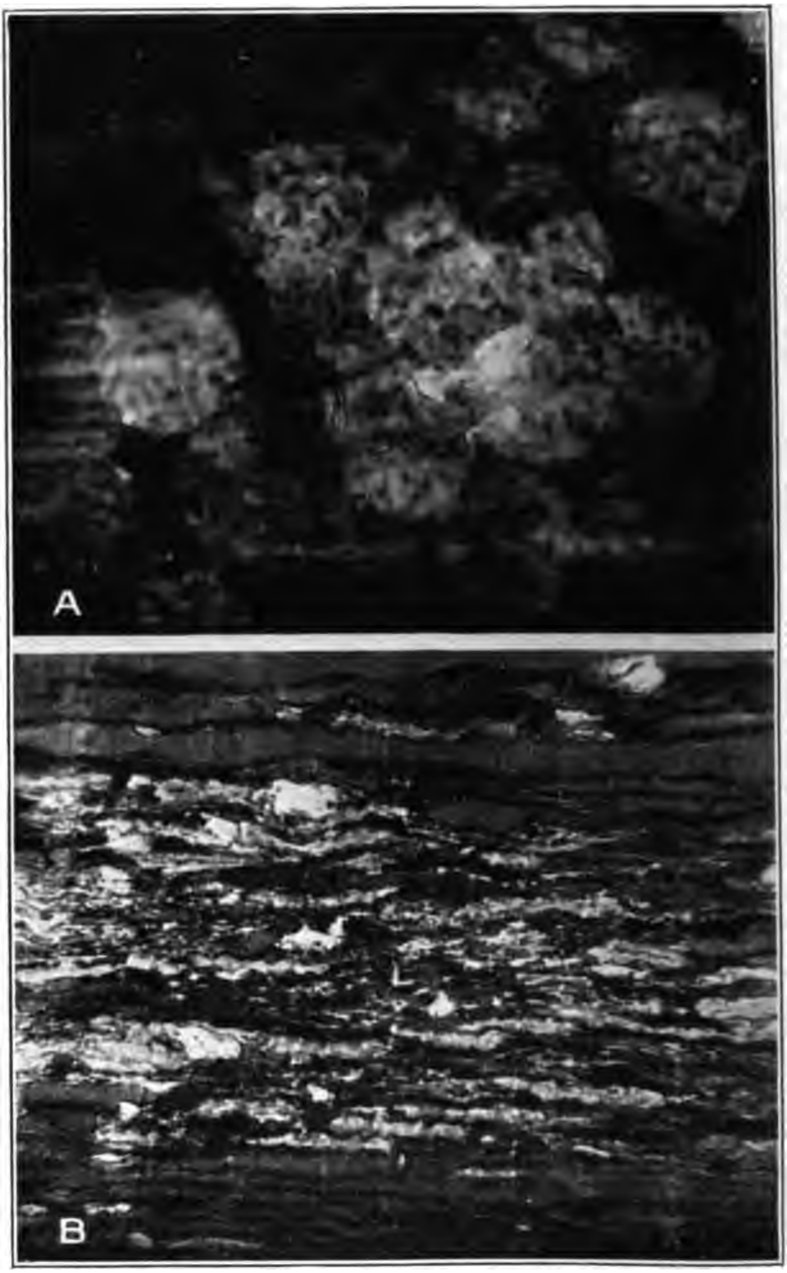
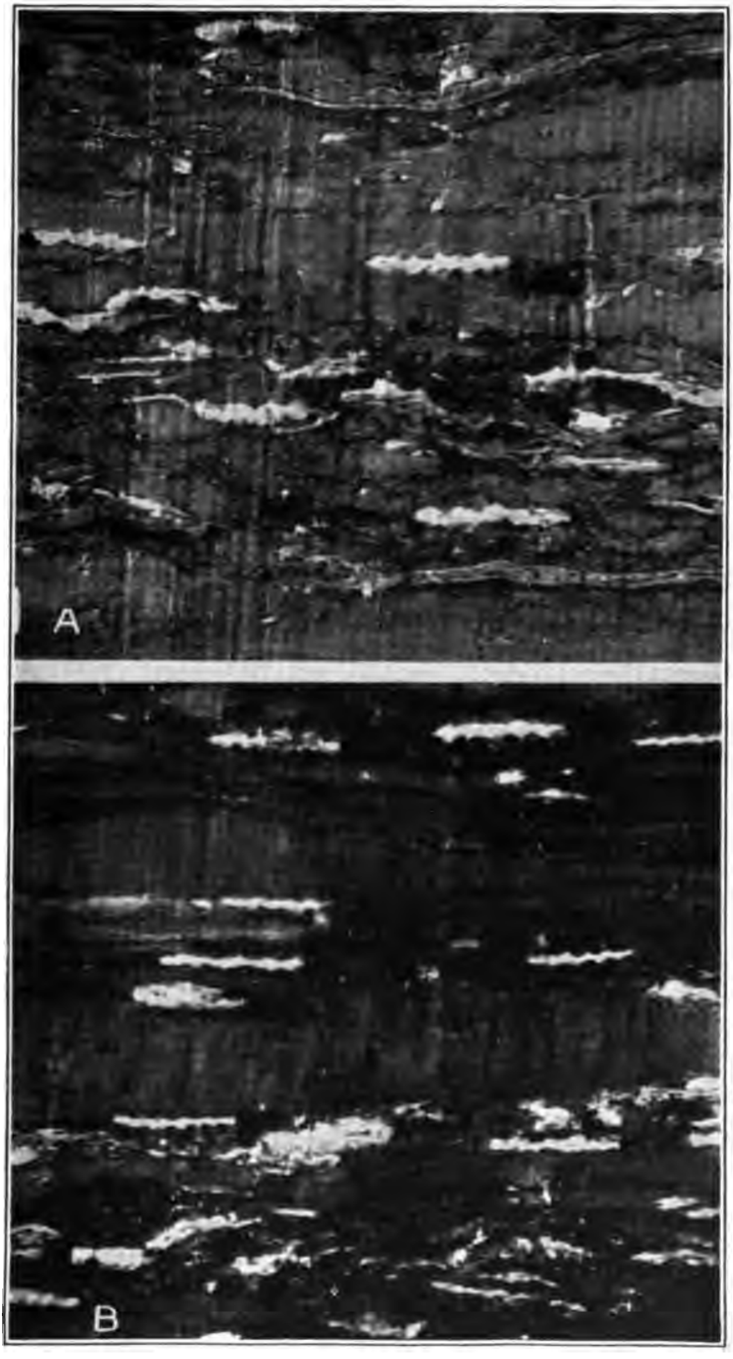


Plate XXVIII.—A, *Thin horizontal section of Sewickley coal, showing characters of the Sewickley spores.*

B, *Part of Plate XXVII showing the spores at higher magnification.*



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B, *Thin cross-section of Sewickley coal from the Belmont mine at Flushing, Ohio, showing same as A.*

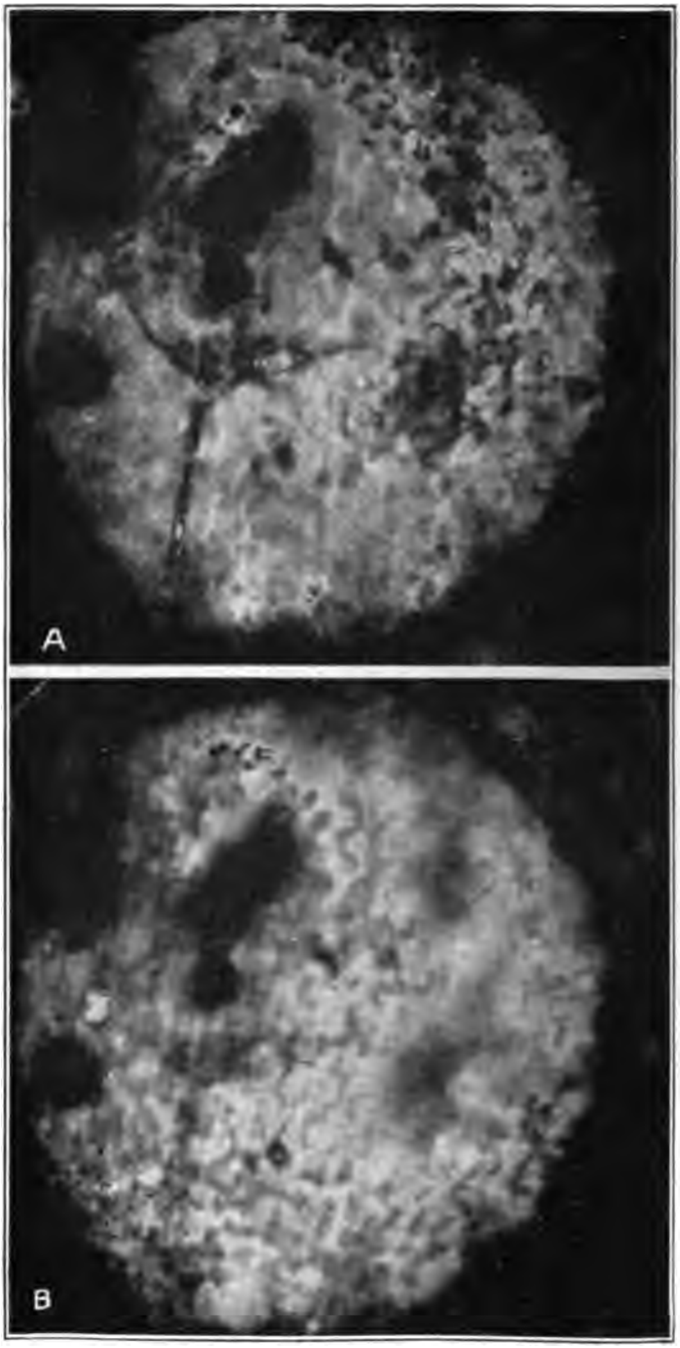
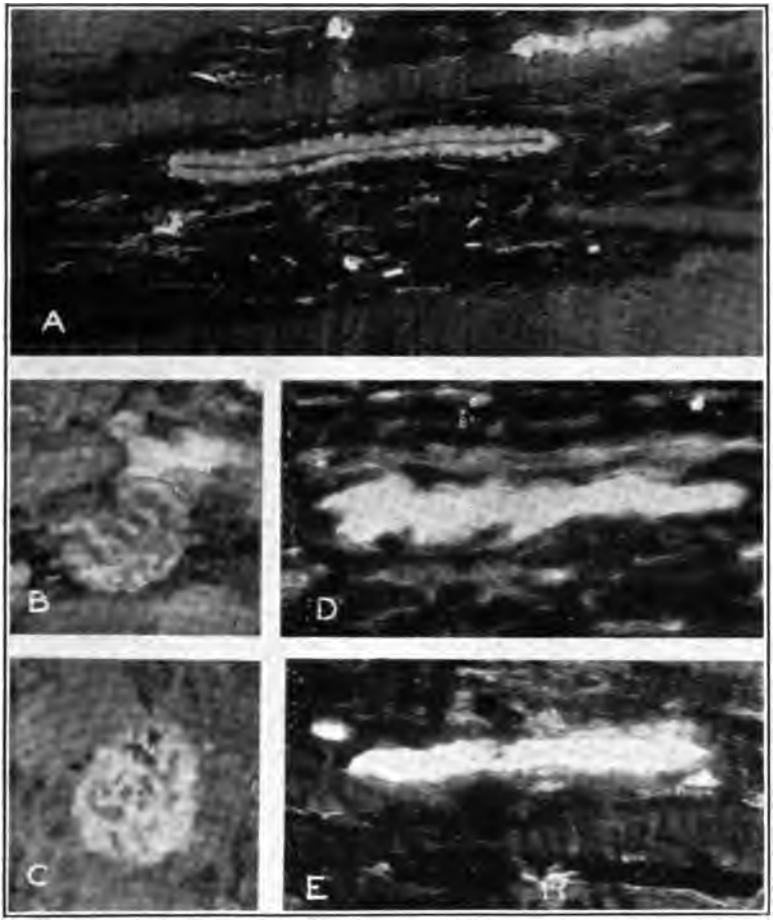


PLATE XXX.—A, *Thin horizontal section of large, highly sculptured spore in the Sewickley coal, found also in the Redstone coal.*

B, *Horizontal section of A at slightly different focus to bring out more of the sculpturing of the surface.*



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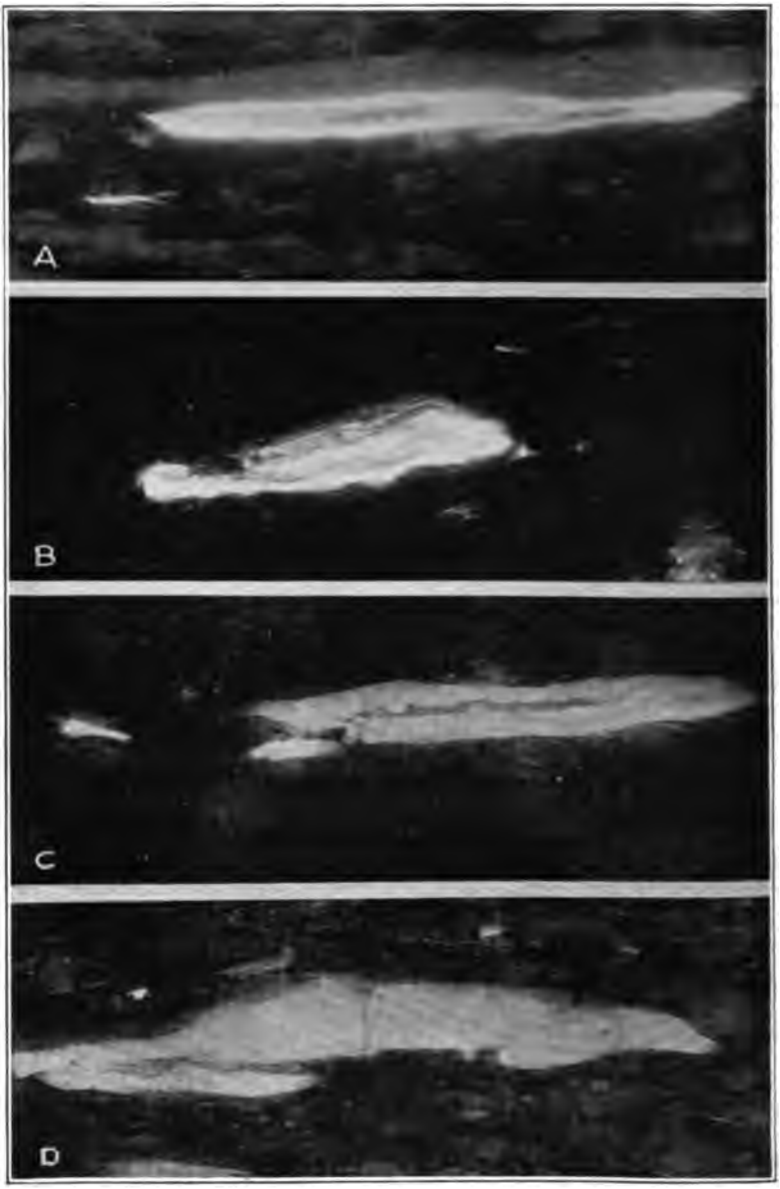
B *and* C, *Horizontal sections of the Sewickley spore.*

D *and* E, *Cross-sections of the Redstone-Sewickley spores.*



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Bulletin 10

COAL-MINING INVESTIGATIONS

UNDER AUSPICES OF

CARNEGIE INSTITUTE OF TECHNOLOGY,
U. S. BUREAU OF MINES, AND
ADVISORY BOARD OF COAL-MINE OPERATORS AND ENGINEERS.

CORRELATION OF COAL BEDS OF THE ALLEGHENY FORMATION OF WESTERN PENNSYLVANIA AND EASTERN OHIO.

By

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Bureau of Mines;

and

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Carnegie Institute of Technology.

CARNEGIE INSTITUTE OF TECHNOLOGY,
PITTSBURGH, PENNSYLVANIA,
1924.

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PREFACE.

In furtherance of a resolution adopted at Pittsburgh on May 27, 1919, at a conference of leading representatives of the coal-mining industry and the President of the Carnegie Institute of Technology, the President of the Institute entered into a cooperative agreement on June 1, 1919, with the Director of the U. S. Bureau of Mines, whereby full advantage could be taken of the Bureau's laboratories, equipment, and library, as well as of the advice and instruction of its technical staff, for the carrying on of fellowships in coal-mining investigations.

To carry out this new program, the Cooperative Mining Courses in the Department of Mining and Metallurgical Engineering, College of Engineering, of the Institute was organized. The course in mining engineering covers four years, and leads to the degree of Bachelor of Science. The two-year course in coal mining is planned to prepare men with a certain amount of practical experience for executive positions. The four-weeks intensive summer course in coal mining is designed for miners who aspire to be firebosses and mine foremen. In a large measure, the mining, oredressing, and coal-washing laboratories at the Institute have been equipped gratuitously by various manufacturers of mining machinery and appliances .

Cooperative studies through research fellowships were initiated in the fall of 1920. The Institute selects the fellows, the Bureau of Mines provides the laboratory facilities, and the Advisory Board determines what problems be undertaken, and publishes the reports, after approval and editing by the Bureau.

Four research fellowships paying $750 per year of ten months are supported by the Carnegie Institute of Technology. These fellowships are open to properly qualified graduates of universities and technical schools. Fellowship holders are required to register at the Institute as graduate students, and become candidates for the degree of Master of Science, unless an equivalent degree has been previously earned. The purpose of these fellowships is the solution of problems in mining and the utilization of coal.

The primary object of this cooperation of the Carnegie Institute of Technology, the U. S. Bureau of Mines, and the Advisory

Board of Coal Mine Operators and Engineers is the proper education and training of young men for the mining industry. The ultimate object is to bring about better conditions and greater efficiency in mining operations. The decrease in reserves of coal and increasing cost of production make it necessary for mine operators and engineers to take advantage of everything whcih modern science, machinery, and methods can contribute.

EDWARD STEIDLE,
Supervisor, Cooperative Mining Courses,
Carnegie Institute of Technology.

FOREWORD.

This bulletin is the second of the series covering the correlation study of the coal beds of Western Pennsylvania, Ohio and West Virginia. This one includes the five important beds of the Allegheny formation—namely, the Upper and Lower Freeport beds, and the Upper, Middle, and Lower Kittanning beds. Samples of coal were obtained from 37 mines, selected to cover as far as possible the entire area of each coal bed in the three States.

Thin sections of the coal were prepared, examined microscopically, and photographed. A number of new and distinct spore forms were discovered, and these have been described and provisionally named. They should prove of great aid to geologists in the correlation and identification of these coal beds.

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CORRELATION OF COAL BEDS OF THE ALLEGHENY FORMATION OF WESTERN PENNSYLVANIA AND EASTERN OHIO.

By REINHARDT THIESSEN *and* FORD E. WILSON.

INTRODUCTION.

In every part of the Northern Appalachian coal field, as well as in other fields, there exists a need for exact correlation of the coal beds. Confusion is caused by the fact that the beds are given a great variety of local names, and because official geological surveys have not used the same nomenclature for beds known to be the same. In some localities, coal operators do not know what bed they are mining, and the coal buyer or consumer often has no check on the source of his coal.

The past and present tendency in coal mining in the eastern bituminous coal region is to obtain maximum production with the least possible expenditure of money and labor, therefore only the most easily mined and best quality coals near the surface have been worked, and the poorer beds have been ignored. The thickest coals having the best quality are gradually becoming exhausted, and in the future, mining will be more and more in the less valuable surface coals and in those beds which lie several hundred feet deep.

ACKNOWLEDGMENTS.

The authors wish to express their appreciation and obligation to all who have assisted in this work. Included is A. C. Fieldner, superintendent and supervising chemist, Pittsburgh Experiment Station of U. S. Bureau of Mines; Edward Steidle, supervisor of Coöperative Mining Courses, Carnegie Institute of Technology; G. H. Ashley, state geologist of Pennsylvania, and J. D. Sisler, associate geologist of the Pennsylvania Topographic and Geologic Survey; J. A. Bownocker, state geologist of Ohio, and Wilber Stout, assistant geologist of the Geological Survey of Ohio; and officials and miners at the mines where samples were collected.

PREVIOUS CORRELATION WORK.

Stratigraphic correlation in the past has, by necessity, been applied chiefly to the economically important beds, but in the future much correlative work must be done on the poorer and deeper beds.

The problem of correlation is difficult because a few coal beds are continuous or uniform over large areas. Locally several beds are present at an horizon where only one normally occurs. Again, a bed may locally be entirely absent at its horizon. These facts are true of outcropping and sub-surface coal beds. The intervals between coal beds are almost never uniform nor constant, and the intervening strata show great diversity in character as well as variation in thickness and extent. A discussion of the complex stratiography of the Allegheny strata in Pennsylvania has been given by Ashley[1]. It is evident then, that the geologist employing stratigraphic methods may often experience difficulty in correlating certain beds.

White[2] has demonstrated the correlative value of the fossil plants in the rocks accompanying a coal bed. These determinations have a disadvantage in requiring painstaking field work, and the study of a large number of various species of plants.

A microscopic method was employed in this study which possesses certain advantages over other methods of correlation. The coal itself contains the characteristics necessary for identification of the bed. Field work is reduced to a minimum, as only suitable samples of coal from the bed or mine in question are required. Diamond-drill cores can also be used. Sections are prepared and examined microscopically in the laboratory. The technique required is very similar to that in petrographic work, and results may be obtained quickly.

Turner and Randall[3] have developed a method involving polished opaque sections and differential oxidation to reveal plant and other structures in anthracite. They suggest that correlation of anthracite beds may be possible by means of these structures. This method may also prove of value in semi-bituminous coals, or coals that are too opaque to be transparent in thin sections. For ordinary bituminous coals, however, quicker and more satisfactory results are obtained with thin sections.

A great deal of correlation work in western Pennsylvania and eastern Ohio has been done by State and Federal geological surveys, employing stratigraphic and paleontological methods.

Thiessen[4], in 1913, after developing the technique of preparing coal thin sections, found that various coal beds contained different spores, and in 1920 suggested[5] the possibility that the different spores might be used in correlative work.

---

[1] Ashley, G. H., Stratigraphy of Southwestern Pennsylvania, Allegheny Formation: Report of Topographic and Geologic Survey Commission of Pennsylvania, 1906-1908, 1908, pp. 165-189.

[2] White, David, The Stratigraphic succession of the fossil Floras of the Pottsville formation in the Southern Anthracite Coal Field, Pennsylvania; U. S. Geol. Survey, 20th Annuual Report, Part 11, 1900, pp. 749-930.

[3] Turner, H. G. and Randall, H. R., A preliminary report on the microscopy of anthracite coal: Jour. of Geol., vol. 31, No. 4, May-June, 1923, pp. 306-313.

[4] White, David, Thiessen, Reinhardt, and Davis, C. A., Origin of Coal: Bull. 38, Bureau of Mines, 1913, pp. 218-289.

Thiessen and Voorhees[6], in 1922, made a microscopic study of the so-called Thick Freeport coal bed in Allegheny, Westmoreland, and Butler counties, Pennsylvania. Their investigation showed that there is a variation in the composition of the bed vertically, but none horizontally. Several spores were found in the bed that differed from spores found in other beds examined at that time.

Thiessen and Straud[7], in 1923, studied the beds of the Monongahela formation in western Pennsylvania, eastern Ohio, and West Virginia. They found it possible to characterize and identify each of the three beds by a study of the constituents seen in thin sections.

The present paper sets forth the results obtained in a similar, although more or less preliminary, microscopic study of the coal beds of the Allegheny formation. Descriptions of the Monongahela spores have been included in the Appendix, so that comparisons may be made with the Allegheny forms.

MICROSCOPIC METHOD OF CORRELATION.

BASIS OF THE METHOD.

The history of the Carboniferous period in Pennsylvania may, in general, be considered as a succession of swamps containing luxuriant vegetation. Alternating with the periods of swampy conditions there were depositions of sediments which buried the swamps. The accumulated vegetable matter in these swamps formed our present coal beds.

The present method of correlation is based upon the assumption that during the intervals between the laying down of the various coal beds at a given place, the coal-forming plants or their societies became changed. As a result of the change in the plants, the spores and other structures now found in coals should likewise show differences. This assumption is proven correct when spores in various beds are found to differ, and a certain spore or spores may characterize a certain coal bed.

The same plant may be expected to have survived long enough to have contributed to more than one coal bed. Certain spores actually do exist in two or more beds. Usually, however, the relative abundance of the spore varies.

---

[5] Thiessen, Reinhardt, Structure in Paleozoic bituminous coals: Bull 117 Bureau of Mines, 1920, pp. 71-72.

[6] Thiessen, Reinhardt, and Voorhees, Anson W., A microscopic study of the Freeport coal bed, Pennsylvania; Carnegie Inst. of Technology, Coal Mining Investigations, Bull. 2, 1922, 75 pp.

[7] Thiessen, Reinhardt, and Staud, J. N., Correlation of the coal beds in the Monongahela formation of Ohio, Pennsylvania, and West Virginia; Carnegie Inst. of Technology, Coal Mining Investigations, Bull. 9, 1923, 64 pp.

The plant society which contributed to a particular bed is assumed to be essentially uniform throughout the area of the swamp, so a horizontally non-variant spore content for a bed results.

A discontinuity of a swamp or a non-uniform flora explains why, in some cases, a coal may have a somewhat varied spore content in different localities. Occasional individuals of almost any of the spores described for one bed may be found in another, and additional types of spores may be present. The predominant or distinctive spores and their relative abundance are considered as the best criteria for correlation work.

The greatest difficulty in this study was in obtaining samples whose horizon and stratigraphic correlation was definitely known.

COLLECTION OF SAMPLES.

Whenever possible, samples were taken from working faces of the mines. Blocks representing a continuous strip from floor to roof were cut from the bed, and each block was separately bagged and labeled. By this means the exact position of any sample in the bed is known for future work. Where it was not possible to enter the mine, samples were taken from mine cars or at the tipple.

Samples for this study were collected in October, November, and December, 1923, and in May, 1924. A total of 38 mines, well distributed in the coal-mining districts, were sampled.

A line drawn through Connellsville and Punxsutawney, Pennsylvania, marks approximately the eastern boundary of coals suitable for thin sections. East of this line the coal is too opaque and too brittle, and the plant remains, including spores, are not well preserved. For this reason the eastern part of the beds of the Allegheny formation in Pennsylvania are not shown in the maps (Figures 1, 2, 3, 4).

PREPARATION OF THIN SECTIONS.

The preparation of thin sections of bituminous coal is essentially identical with the process employed for ordinary rock or petrographic thin sections. A block of suitable size is ground and polished on one side to give a plane face about ½ by ¾ inch in size. This surface is dipped in molten paraffin for a few minutes, the surplus paraffin is wiped off, and the surface cemented to a glass object slide by means of a canada balsam-marine glue cement, made by heating approximately two parts of hard marine glue with three parts of canada balsam to the proper hardness. Waterproofing with paraffin is necessary because otherwise the coal would absorb water during the final grinding, swell up, and leave the glass slide.

The block of coal is then ground to the required thinness, usually 3 to 10 microns[8], and polished. The last part of the grinding is done on a very fine blue-stone. The final step is to cement a cover glass over the section.

CONSTITUTION OF COAL.

Bituminous coal, as observed in a hand specimen, is composed of alternating horizontal bands of bright and dull luster, and thin layers of a material resembling charcoal (mother of coal). On closer examination, the dull bands are found to be made up of thinner bright bands in a matrix or ground mass of dull material. All of the bright bands are lenticular. They represent woody matter of the coal-forming plants, and their substance is called anthraxylon. In a thin section, anthraxylon appears as reddish-yellow to reddish-brown translucent bands or layers. In all cases it shows evidence of the original plant-cell structure. In general, coal becomes more anthraxylous descending from the roof to the bottom of a bed.

The dull matrix, called attritus, is a plant debris containing a variety of components. Among these are the degradation products of plant tissues, spores, and pollen grains, cuticular matter, resinous particles, crystals and masses of pyrite, and more or less highly carbonized parts. The more attritious coal is at the top.

The spores of certain of the coal-forming plants are the most conspicuous, and for correlative purposes the most important objects seen in a thin section of coal.

The *Equisetales*, represented by the calamites or giant horsetails, and the *Lycopediales*, represented by lepidodendrons, bathrodendrons, and sigilarias, were the dominant coal-forming plants. Of lesser importance were the *Pseudeborniales* and *Sphenophyllales*. All of them produced, during one stage of their reproductive cycle, enormous numbers of spores.

Certain groups produced two types of spores—namely, microspores and megaspores—each of which had a different function. As it is impossible to distinguish these kinds of coal, they are here arbitrarily divided into microspores and megaspores on the basis of size. Those from 10 to about 150 microns in diameter are classed as microspores; the larger ones which may be as much as 3000 microns in diameter, belong in the megaspore group.

In the last stages of the development of the spores, two divisions of the cell occur simultaneously, and give rise to four tetraspores. This process forms a triradiate or tetrasporic mark on the spore, which distinguishes true spores from pollen.

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[8] One micron equals 1/1000 millimeter or 1/25000 inch.

The living spore consists of a protoplastic central part, a thin inner wall or entine, and a thick outer wall or exine. The spores are represented in coal by these exines, all of which have a discoid shape due to pressure and collapse. In horizontal thin sections they are bright yellow to reddish-yellow in color, have a round oval or rounded-triangular outline, and usually possess a distinctive surface configuration. These objects in coal are therefore only a part of the spore, the outer wall or exine, but for brevity they will be called spores.

In making a vertical section, the discoid spores are cut across at various distances from the center. Therefore, in such sections the apparent length is usually less than the true diameter of the spore, while the cell-walls will show their actual thickness.* The form of outline depends upon the shape of the spore and its surface configuration. The inner cavity is represented by a dark line.

Gymnospermae, represented by *Cysadofilicales* and *Coniferales*, also grew in the Paleozoic swamps. Large numbers of their pollen grains are found in coal. These pollens are very similar in appearance to the true spores, as they have the same color, size, and discoid shape. However, they are exceedingly thin, their surface is always smooth, and they never have the tetrasporic mark. In horizontal section they have an oval outline, and usually a slit parallel to the long dimension. Many of the slits have a short cross slit at or near one end.

It is manifestly impossible to determine the genus or specie names for the plants which produced the spores and pollen in coal, although such names have probably already been given on the basis of other parts of the plants. Moreover, it is entirely possible that the same type of spore may have been produced not only by different species and genera but also by different families. Therefore, the spores in coals of the Allegheny formation have been designated in this paper by the name of the bed in which they occur, followed by an appropriate descriptive term.

The cuticular matter appears in a vertical thin section as transparent, bright-yellow, narrow bands of indefinite length. One edge is commonly sinuate or wavy, and the cuticles are often much folded.

The term resinous matter includes two kinds of material; one forms lemon-yellow, transparent masses; the other is translucent, of a color like anthraxylon, and occurs as round or oval masses. All of the resinous matter is characterized by homogeneity.

Microscopic pyrite is found in all portions of the coal. It is often in the form of more or less euhedral or well-formed crystals, usually cubes or octahedra. More commonly it is in irregular grains, rounded masses, or finely disseminated very minute particles. In sections, pyrite is opaque by transmitted light and yellow with metallic luster by reflected light.

Various masses in the coal are more or less highly carbonized. In some, which are but slightly darker than the main mass of the coal, there is a complete gradation to entirely opaque bits (mineral charcoal or fusain). This mineral charcoal is prominent in hand specimens, where it usually forms the horizontal fracture surfaces. Cell structure is commonly evident.

Calcite, probably derived from some nearby limestone or calcareous bed, is occasionally found filling cracks or cavities in coal.

THE ALLEGHENY FORMATION.

The Allegheny formation, formerly known as the "Lower Productive Coal Measures," rests upon the Pottsville group, and is overlain by the Conemaugh formation. The relative positions of the formations is given in the following generalized column of coal bed horizons in Ohio and Pennsylvania:

Generalized column of Pennsylvania coal-bed horizons.

Permian.				Western Pennsylvania.	Ohio.	
Paleozoic	Carboniferous	Pennsylvanian	Monongahela	Waynesburg coal	Waynesburg coal	11
				Uniontown coal	Uniontown coal	10
				Sewickley coal	Sewickley or Meigs Creek coal	9
				Redstone coal	Redstone or Pomeroy coal	8a
				Pittsburgh coal	Pittsburgh coal	8
			Conemaugh	Little Pittsburgh coal	Little Pittsburgh coal	
				Elk Lick coal	Elk Lick coal	
				Ames or Crinoidal limestone	Ames limestone	
					Harlem coal	
				Bakerstown coal	Anderson coal	
					Cambridge limestone	
					Wilgus coal	
					Brush Creek limestone	
					Mason coal	
				Mahoning coal	Mahoning coal	
			Allegheny	Upper Freeport coal	Upper Freeport coal	7
				Lower Freeport coal	Lower Freeport coal	6a
				Upper Kittanning coal		
				Middle Kittanning coal	Middle Kittanning coal	6
				Lower Kittanning coal	Lower Kittanning coal	5
				Vanport limestone	Vanport limestone	
				Clarion coal	Clarion coal	4a
					Putnam Hill limestone	4a
				Brookville coal	Brookville coal	4
			Pottsville		Tionesta	3b
				Upper Mercer limestone	Upper Mercer limestone	
					Bedford coal	
					Upper Mercer coal	3a
				Lower Mercer limestone	Lower Mercer limestone	
				Middle Mercer coal	Middle Mercer coal	
					Flint Ridge coal	
				Lower Mercer coal	Lower Mercer coal	3
				Quakertown coal	Quakertown or Jackson Hill coal	2
				Sharon coal	Sharon or Massillon coal	1

The Vanport or Ferriferous limestone, the Ames or Crinoidal limestone, and the Pittsburgh coal are the three great key horizons for correlation of strata in this part of the geologic column, and have therefore been added.

The Allegheny formation in Pennsylvania has an average thickness of 300 feet and in Ohio about 250 feet, made up by sandstone, shale, limestone, and coal. The coal is bituminous, with some cannel.

The general geographic distribution of the formation may be seen in the maps (Figures 1 to 6) of the Kittanning and Freeport beds.

The Monongahela and Allegheny are the most important coal-producing formations in western Pennsylvania and Ohio.

LOWER KITTANNING BED.

(B IN PENNSYLVANIA; 5 IN OHIO.)

The Lower Kittanning horizon lies in the Allegheny formation, between the Clarion, 20 to 45 feet below, and Middle Kittanning, 20 to 45 feet above. Its position is usually definitely known because of the presence of the Vanport or Ferriferous limestone a few feet below. The geographic distribution of the bed in Pennsylvania is shown in Figure 1.

As the bed lies only from 20 to 45 feet below the Middle Kittanning in Ohio, the geographic distribution of the Middle Kittanning shown in Figure 2 serves to show its position in that State.

In Pennsylvania, the bed is uniform and persistent, and is one of the valuable beds in the bituminous district. In Ohio, the Lower Kittanning is mined for shipment and local purposes in Columbiana, Mahoning, Stark, Carrol, Wayne, Tuscarawas, Coshocton, Muskingum, Perry, Jackson, and Lawrence counties.

Local names in Pennsylvania for coals believed to be at this horizon are Miller, Coman, and Blacklick in Cambria County; Dagus or Daguscahonda in Elk County; and Barnet in Bedford and Huntingdon counties, and Bloss in Tioga County.

Similar local names in Ohio are Newcastle in Lawrence County, Leetonia, Creek Vein, Hammondville, Potters Vein, Mineral Point, and Lower New Kensington.

Samples for study of the Lower Kittanning bed were obtained from the following mines:

Mines sampled for Lower Kittanning coal.

Mine.	Place.	County.	State.
Bostonia	New Bethlehem	Armstrong	Pennsylvania
Furnace Run	Kittanning	Armstrong	Pennsylvania
Cadogan No. 1	Ford City	Armstrong	Pennsylvania
Paul	Zanesville	Muskingum	Ohio
Coleman	Leesburg	Mercer	Pennsylvania

SPORES OF LOWER KITTANNING COAL.

The Lower Kittanning coal has one predominant characteristic spore, which so far has not been found in any other bed either in Ohio or Pennsylvania. It will be called the Lower Kittanning biconcave microspore. (Plates I, II, III, IV, and V.)[9]

Description of biconcave microspore.—Diameter, 35 to 40 microns or more[10]; thickness at center, 1 to 3 microns; thickness near edge, 4 to 6 microns; form, biconcave, discoid, disc circular or nearly so; elongated or irregular dumb-bell shaped outline in vertical section; surface, apparently smooth.

No difficulty should be experienced in recognizing this spore, because of its distinctive biconcave form. It may be noted that biconcave spores of similar appearance have been found in certain coals[11] from Alabama, Illinois, and England.

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[9] With the exception of Plates XXIII A and B, all of the photomicrographs in this paper are made with a magnification of either 200 or 1000 times. They are thus uniform with those in Bulletins 2 and 9 of this series.

[10] In the descriptions of spores the metric system of measurement is employed: millimeter, 0.03937 inch, or approximately 1/25 inch; and the micron, which is one 1/1000 millimeter, or nearly 1/25,000 inch.

[11] Thiessen, Reinhardt, Structure in Paleozoic bituminous coals: Bull. 117, Bureau of Mines, 1920, 250 pp. (Plates CXXXVIII and CXXXIX).

The distance between New Lexington, Ohio, and New Bethlehem, Pennsylvania, is more than 100 miles, yet the spores in this bed at both extremes of the territory are similar. This would indivate a very uniform flora during Lower Kittanning times.

A few smooth-surfaced, usually thin-walled, microspores with a diameter of 20 to 30 microns are also present (Plate VI), but these have no diagnostic value. The same or similar spores occur also in each of the other beds of the Allegheny formation. Pollens of similar appearance also occur.

A number of megaspores are also found in this bed, as in the other beds examined, but as these spores have not been studied discriminately, no further description is given. Plate VII, magnified 200 diameters, shows the relative size of these spores.

The relatively large size of these megaspores is seen by the fact that if magnified 1000 times, as are the other individual spores shown, they would appear 6 to 11 feet in diameter.

MIDDLE KITTANNING BED.

(C IN PENNSYLVANIA; 6 IN OHIO.)

The Middle Kittanning lies between the Lower and Upper Kittanning beds. In Pennsylvania it is usually so thin and of such poor quality that it is of no economic importance, although it is worked in some localities.

In Ohio, the Middle Kittanning is a valuable coal, being first in value of coal production, like the well-known Hocking Valley coal in Hocking Valley. The outcrop of the bed is shown in Figure 2.

Local names in Ohio for beds believed to be Middle Kittanning are Great Vein, or Hocking Valley in Hocking Valley; Osnaburg in Stark County, Pike Run and Dennison in Tuscarawas County; Coshocton, Upper Zanesville, Upper New Lexington, Nelsonville, Straitsville, Carbondale, Mineral City, Upper Zaleskie, Washington Furnace, and Sheridan.

For microscopic study of the bed, samples were taken from the following Ohio mines:

Mines sampled for Middle Kittanning coal.

Mine.	Place	County.
Maxwell Brothers	New Lexington	Perry
Euga	New Lexington	Perry
Cresmas	Crookesville	Perry
Schnell & Schumacher	Crookesville	Perry
Paul	Zanesville	Muskingum
Penn	Roseville	Muskingum
Warwick No. 5	Coshocton	Coshocton
Warwick No. 4	Coshocton	Coshocton
Scott	Dennison	Tuscarawas
Indian Hill	Uhrichsville	Tuscarawas
Laurel Valley	Stillwater	Tuscarawas
Tippecanoe	Tippecanoe	Harrison

No samples were obtained from this bed in Pennsylvania.

SPORES OF MIDDLE KITTANNING BED.

The Middle Kittanning bed is characterized by containing few types of spores. A pitted spore is characteristic and generally distributed over the entire bed, and generally predominates. It will be called the Middle Kittanning pitted microspore. (Plates VIII and IX).

Description of pitted microspores.—Diameter, 20 to 30 microns; disc, often slightly oval; walls, from 5 to 10 microns thick; general shape, discoid, quite regular; surface, covered with irregular, rounded, shallow pits or depressions; in vertical sections, outline sinuate or wavy, and dark line or band indicating central cavity distinct; good tetrasporic marks occasionally seen on disc.

It may be distinguished from the Pittsburgh spore by its larger size and different surface configuration. It is very similar to the Sewickley spore, but may be distinguished by its somewhat larger size and thicker walls. From the Upper Freeport pitted spore it may be differentiated by its generally smaller size and more regular outline in vertical thin sections.

In the Dover area of this bed a second smooth thick-walled microspore is very pronounced and characteristic, and easily serves to distinguish it from the Upper Freeport bed above it. In the Coshocton area this spore is far less abundant, and in the Hocking Valley districts it is only sparsely represented, and is therefore unimportant.

UPPER KITTANNING BED.
(C′ IN PENNSYLVANIA)

The Upper Kittanning horizon lies between the Middle Kittanning and Lower Freeport. A large quantity of cannel in Pennsylvania comes from this horizon. The bed is not persistent over large areas, but is patchy, as shown by Figure 3.

Local names in Pennsylvania for coals believed to be at this horizon are Darlington and North Washington cannel in Beaver County; Woodland cannel in Clearfield County; Big Bed in Center County; Cement in Cambria and Somerset counties; Barnettstown in Broad Top field; No. 4 or Creek in Butler County. There are no names in Ohio for coal at the Upper Kittanning horizon.

The only sample of Upper Kittanning coal obtained was from the Bostonia No. 8 mine at New Bethlehem, Pennsylvania. Here about 7 feet of cannel overlies about 2½ feet of bituminous coal.

SPORES OF KITTANNING BED.

The Upper Kittanning coal is characterized by three spores—namely, the Upper Kittanning finely pitted microspore (Plate XI), the large zoned microspore (Plate XII), and the Upper Kittanning deeply pitted microspore (Plate X B and C).

Description of finely pitted spore.—Diameter, 30 to 40 microns; cell walls, about 1 micron thick; discoid, very regular, occasionally folded upon itself; disc circular or oval; surface, covered with very fine pits; outline in vertical thin sections, finely sinuate or wavy; found only in this bed. (Plate XI).

Description of large zoned spore.—This is a large spore with a main central thicker spore part encircled by a thin zone or outer ring. The overall diameter of the spore is approximately 85 to 90 microns; the diameter of the central thicker part is approximately 45 to 50 microns; the thickness of the central part is 2 to 5 microns, and the thickness of the outer zone is less than 1 micron. The surface is smooth. Its appearance in cross and horizontal sections is well shown on Plate XII. Apparently in the living state the central part was the spore proper, while the surrounding much thinner ring functioned as a wing. A similar spore is also found in the coal from Shelbyville, Illinois, lying in the "barren measures" in the McLeansboro formation, and in the coal reported to have come from the Brookville bed in Mercer County, Pennsylvania.

Description of deeply pitted spore.—A peculiarly deeply-pitted spore is found in relatively small numbers in both the coal and the cannel, but more often in the latter than in the former. In cross section they resemble a hairy caterpillar. It will be called the Upper Kittanning deeply pitted microspore. (Plate X B and C).

The diameter of this spore is 30 to 50 microns; thickness of cell wall, 3 to 5 microns; form, discoid, regular; disc circular or slightly irregular; surface, apparently covered with deep pits, reaching nearly to the center of the spore wall shown in the illustrations.

The cannel contains a variety of spore forms. The greatest number are smooth-walled spores with thick or thin walls. Here are present also a few pitted spores like those of the Middle Kittanning coal. (Plate IX). Another form rarely found is the pear-shaped spore described with the Upper Freeport spores. (Plate XXIII).

LOWER FREEPORT BED.

(D IN PENNSYLVANIA; 6a IN OHIO.)

The Lower Freeport horizon lies between the Upper Kittanning below and the Upper Freeport above. In Pennsylvania (see Figure 4) this bed is valuable as a coal producer, but in Ohio it is but little worked.

Local names in Pennsylvania for coal believed to be at this horizon are Moshannon in Clearfield and Center counties; Limestone in southern Cambria County, and Dudley in the Broad Top field. In Ohio it may be the Whan coal of Lisbon, Rogers of Columbiana and Jefferson counties, Hatcher in Lawrence County and Rodger.

For the microscopical study of the Lower Freeport bed, samples were obtained from the following mines in Pennsylvania:

Mines sampled for Lower Freeport coal.

Name.	Place.	County.
Adrian No. 1	Punxsutawney	Jefferson
Bostonia No. 6	New Bethlehem	Armstrong
Cadogan No. 4	Cadogan	Armstrong

Coal from the Adrian mine is too opaque, and the spores are now too poorly preserved to be of value in correlation. To a lesser degree that is true of the Bostonia mine. Exact microscopic study of this bed is therefore based largely upon coal from the Cadogan mine, but comparisons have been made with samples collected during previous years from other localities. Coals from the Upper and Lower Freeport beds, so far as they have been studied, appear to have several spores in common. The Lower Freeport coal has relatively only a few kinds of spores, while the Upper Freeport has a considerable number of different kinds, this rendering the main distinction between the two coals.

SPORES OF LOWER FREEPORT BED.

A relatively small smooth-walled spore is predominant in this coal. It is relatively thick-walled and somewhat variable in size; its mean diameter varies between 20 and 25 microns, and between 3 and 5 microns in thickness. (Plate XIV A).

A larger finely pitted spore appears to be invariably present in small numbers. This spore is shown in Plates XV A and B.

Its diameter is about 60 microns, with a thickness of 4 microns or total thickness of disc of 8 microns. In cross sections, edges appear very finely serrated, due to very fine echinate elevations on the surface.

The Upper Freeport pitted spore (Plate XVIII)) is also found in the Lower Freeport bed, but only in the upper few inches. The Upper Freeport ridged spore (Plates XXII A and B) is quite prominent in the Lower Freeport bed.

The Upper Freeport pear-shaped spore (Plate XXIII) was not observed in the Lower Freeport. Various thin-walled microspore pollens and megaspores are present in relatively small numbers.

UPPER FREEPORT BED.

(E IN PENNSYLVANIA; 7 IN OHIO.)

The Upper Freeport bed is the topmost member of the Allegheny formation. Its geographic distribution is shown in Figures 5 and 6. It is one of the most valuable coal beds in both Pennsylvania and Ohio.

Local names in Pennsylvania for coal beds believed to be at this horizon are Lemon and Cokeyard in Cambria County; Kelly in Bedford and Huntingdon counties; Four-Foot and Five-Foot in Beaver County; and Thick Freeport or Double Freeport or Twin Vein in Allegheny and Westmoreland counties. In Ohio, similar local names are Black Band in Stark and Tuscarawas counties; Big Vein in Salineville; Alexander and Blue Rock in Muskingum County; Waterloo in Gallia County; Bayley's Run and Norris in the Hocking Valley; and Del Roy, Sherrodsville, and Cambridge.

For microscopic study of the Upper Freeport bed the following mines were sampled:

Mines sampled for Upper Freeport coal.

Mine.	Place.	County.	State.
Craborchard	Freeport	Harrison	Ohio
Maple Leaf	Uhrichsville	Tuscarawas	Ohio
Walnut Hill	Pleasant City	Guernsey	Ohio
Moss	Pleasant City	Guernsey	Ohio
Romine	Zanesville	Muskingum	Ohio
Anderson	Zanesville	Muskingum	Ohio
High Shaft	Steubenville	Jefferson	Ohio
Amsterdam No. 1	Amsterdam	Jefferson	Ohio
O. and P. No. 2	Amsterdam	Jefferson	Ohio
Burris	Cambridge	Guernsey	Ohio
Elm Tree	Cambridge	Guernsey	Ohio
Vogeley	Butler	Butler	Pennsylvania
Florence	Punxsutawney	Jefferson	Pennsylvania
Bostonia No. 10	New Bethlehem	Clarion	Pennsylvania
Cadogan No. 3	Cadogan	Armstrong	Pennsylvania
Kerr No. 2	Freeport	Allegheny	Pennsylvania
Cannelton	Cannelton	Beaver	Pennsylvania

SPORES OF UPPER FREEPORT BED.

The Upper Freeport coal contains a larger quantity of spore matter contributed by a larger number of types of spores than in any of the coals immediately below it. But in this profusion of spores, several types can be singled out that are characteristic and predominant. These characteristics hold true over the whole area investigated both in Ohio and Pennsylvania. (Plates XVI to XXIII).

The predominant and characteristic spore of this bed is the Upper Freeport pitted microspore. (Plates XVIII and XIX).

Description of pitted spore.—Diameter, 25 to 35 microns; thickness of cell wall, 3 to 5 microns; form, discoid, commonly irregular; disc circular, oval or irregular, outline in horizontal thin sections usually sinuate or irregular; outline in vertical thin sections coarsely sinuate or irregular; surface covered with irregular, rounded pits or depressions; found in all parts of the bed, but most abundant near the top.

This form is very similar to the Middle Kittanning pitted spore. It appears to differ by being, on the average, somewhat larger, and by showing a greater number of irregular shapes in vertical thin sections deeper loby and course sinuation.

A second predominant spore is a rather small, smooth thick-walled spore. (Plate XX A and B). Its diameter is approximately between 25 and 30 microns, and the total thickness of the two walls of the disc between 2 and 3 microns. It is circular to oval in make, and is smooth-walled.

Description of smooth-walled spore.—Diameter 25 to 30 microns; thickness of cell wall, 1 to 15 microns; total thickness, 2 to 3 microns; surface smooth; shape, circular to oval. Predominant throughout the bed.

A third spore found commonly is the Upper Freeport ridged spore. (Plates XXI A, B, and C).

Description of ridged spore.—Diameter, 50 to 60 microns; thickness of cell walls, about 5 microns; form, discoid; outline in horizontal thin sections, rounded; surface, smooth; a few ridges running across the disc give the spore a distinct outline in vertical thin section.

A spore with a very distinct form, to be called the Upper Freeport pear-shaped spore, appears irregularly throughout the bed. As a whole they are but few in number, but occasionally appear in large numbers sporadically. (Plates XXII A and B)).

Description of pear-shaped spore.—Diameter, 30 or more microns; cell wall varies in thickness from 1 micron at the thinnest part to 10 microns at its thickest; form, roughly bilaterally symmetrical; surface smooth. The best development of this form was found in the coal from the Craborchard mine, Freeport, Ohio, and in the Thick Freeport area. The Upper Kittanning cannel from the Bostonia mine contains a few individuals of this or a similar spore.

An unusually large array of nondescript microspores and pollens are present. Plate XXIII shows several large smooth-walled megaspores taken with special low magnification of 50 times to show a complete spore. The tetrasporic mark is distinctly shown in Plate XXIII A. It should be noted that this is a small individual with a diameter of only 500 microns; other megaspores have a diameter of 3000 microns.

PROBLEMS IN CORRELATION.

It is quite apparent that certain constituents in the coals, particularly the spores, furnish a means for the correlation of coal beds. This, however, does not furnish an easy method in all cases. In some beds it is surprisingly easy and simple, while in others it is difficult and only possible with the most careful and minute examination. Between these two extremes are to be found cases of various expediencies and complications.

The study of correlation of coal beds by the microscopic study of its plant constituents has only begun, and requires considerably more study and experience before it can be classed as a generally applicable method.

The microspores in the coal have mainly been used in this study, the megaspores having been left out of consideration for the time being. The general nature of the coal has been used in a limited manner. Stratigraphic relationships have been considered wherever available.

The general nature and appearance of the coal is of considerable value for identification, particularly locally where the coal beds are close together, and in the same state of "metamorphism" or physical condition. Coal in widely separated areas in the same bed or in different beds, may be in varying states of metamorphism, and differ in their general nature on this account. A clear example of this difference in the coal of the same bed is to be found in the Pittsburgh bed. The coal changes gradually in physical and chemical character, so that coal from the extreme western part of the bed is totally different from that of the extreme eastern part. The constituents comprising the coal, however, are the same. Differences due to metamorphism must always be taken into consideration when comparisons are made as to the general nature of the coal.

The cell structure of the anthraxylon or constituents of coal derived from the woody parts of plants have not been studied with a view to correlation purposes, and have not been made use of in this study. Whether the cell structure will be of importance in correlation work remains to be seen, but it would seem to be of considerable value.

Much difficulty was encountered in this study in not having enough type samples of each bed. This was particularly true of the sporadic beds in which a good means for correlation is most desirable. A number of type localities in the Lower Kittanning bed, for example, were pointed out in Ohio, but on examination of the coal in the laboratory, one only proved to be Lower Kittanning coal. Fortunately, the characteristics of the coal are so distinct that mistakes can hardly be made. For the Lower Freeport in Ohio, all of the samples supposed to be from type Lower Freeport localities proved to be Upper Freeport coal.

In some beds one or a few representative samples are sufficient identify the coal safely, as in the coal from the Pittsburgh bed or the Lower Kittanning bed, among others. In most cases, representative samples should be taken from the floor to the roof at certain intervals, and in a few places at shorter intervals; the safest method is to take the samples from bottom to top at short intervals. Then the chances of getting representative samples are better and all the characteristics to be found in the coal. A sample from the Pittsburgh bed taken near the floor would not be a representative sample of the whole bed, though it might be a representative sample of the bottom coal. In such a sample the characteristic spore may be absent, as they often are, and a safe determination could not be made; or a sample may be taken from an outcrop, or from a part of the bed with a shallow covering, in which case the characteristics of the spore might have been destroyed through weathering, although not necessarily so, and a safe determination could not be made. Occasionally also it is necessary to compare the coal not only with the same coal from type samples, but with type samples of coal from other beds, containing similar characters.

The stratigraphic relationships of the coal bed should always be studied, and may be absolutely essential. For example: in the Sewickley bed of the Monongahela formation and in the Middle Kittanning of the Allegheny formation, the predominant and characteristic spores are quite similar. Very accurate examinations are necessary to discriminate between them, should it be necessary to correlate microscopically these two coal beds, without their stratigraphic relationships being known. If one is known to be from the upper part of the Monongahela formation and the other from the lower part of the Allegheny, no difficulty would arise in their classification.

CORRELATING THE LOWER KITTANNING BED.

The Lower Kittanning coal contains characteristics in the presence of the biconcave spores (Plates I to V) that are unmistakable. The characteristic appearance of these spores both in cross and horizontal sections are quickly and easily noticed. On the whole these spores are fairly abundant, particularly in the upper part of the bed, and are easily the most predominant ones. A second spore, shown in Plate VI, is also prominent, and should be taken into consideration. As no other coal in the neighborhood of this horizon contains the biconcave spore, it is easily and safely identified.

CORRELATING THE MIDDLE KITTANNING BED.

The Middle Kittanning coal is recognizable by the Middle Kittanning pitted spore, shown in Plates XIII and IX. This spore is easily the predominant spore and is recognizable through its wavy outline in cross section, or pitted or pocked appearance in horizontal section. This spore is accompanied by a second rather small smooth spore, very similar to the smooth spores found in the Lower and Upper Freeport beds. In the Dover area this smooth spore is predominant, and helps to distinguish the Middle Kittanning coal from the Upper Freeport coal above it. In the Coshocton region it is present in considerably fewer numbers, and in the Hocking Valley region it is found in relatively small numbers. Unfortunately, the Middle Kittanning pitted spore is similar to the Upper Freeport pitted spore, and it requires some care to distinguish between them. The smaller size of the Middle Kittanning, the somewhat larger lobing, and the more sharply contoured sculpturing of the Upper Freeport spore, help to distinguish between them. In sections where these differences in character are the only means of distinction, exact measurement must be resorted to. The Middle Kittanning measure between 20 to 30 microns in diameter and the Upper Freeport spore between 25 and 35 microns, so to distinguish between them requires close scrutiny. The Middle Kittanning was not sampled nor found in Pennsylvania.

CORRELATING THE UPPER KITTANNING BED.

The Upper Kittanning coal was not found in Ohio. In Pennsylvania it appears sporadically, and is mined to some extent. This coal is usually overlain by a considerable thickness of cannel, which was not studied minutely.

The coal contains few kinds of spores. One, a relatively large finely pitted microspore, 30 to 40 microns in diameter (Plate XI), and another, a very large zoned microspore (Plate XII), should identify the coal readily. Unfortunately, this coal was sampled only at one locality, and as it has not been determined whether these spores are constant or not, it is very desirable to examine it further. The large zoned microspore is also found in a coal reported to have come from the Brookville coal in the Mercer formation, where it forms one of several characteristic and dominant spores. It also is a prominent spore in the coal from the No. 2 bed in the McLeansboro formation of Illinois.

CORRELATING THE FREEPORT BEDS.

In Pennsylvania it was found an easy matter to distinguish the two Freeport coals from the coals from beds below them and the Pittsburgh coal above, by means of the characteristic spores that predominate in each of these coals. It is, however, a difficult matter to distinguish between the Upper and Lower Freeport coals themselves.

In Ohio, no Lower Freeport coal was encountered as far north as Amsterdam and Uhrichsville, although farther north and east it is possibly present.

The Upper Freeport is characterized by numerous spores and the large number of different types of spores—namely, the predominant Upper Freeport pitted spore (Plate XVIII), the predominant Freeport smooth spore (Plate XX), the characteristic Upper Freeport pear-shaped spore (Plate XXII), and the ridged spore (Plate XXI). The Upper Freeport pitted spore and the smooth-walled spore are easily the two predominant spores. The pitted spore is easily distinguished, and is found throughout the bed from top to bottom, more abundantly toward the top, except in the Thick Freeport area where it is more abundant in the top of the lower bench coal. Unfortunately, this same type of spore is also present in the upper part of the Lower Freeport coal, although in relatively small numbers. The pear-shaped spore is not uniformly present but appears sporadically, and can not always be depended upon; but it has not been found in any other bed except in very small numbers in the cannel of the Upper Kittanning bed.

The Lower Freeport bed contains relatively few spores represented by only a few types. A large finely pitted spore (Plate XV) is fairly abundant, and is found only in very small numbers in the Upper Freeport. The pear-shaped spore has not been found in the samples of the Lower Freeport examined.

The two Freeport coals may therefore be distinguished from one another by large number of spores and pollens, the larger number of types and the larger number of the large pitted spore in the Upper Freeport bed; and the smaller number of spores and kinds of spores, and absence of the pear-shaped spore in the Lower Freeport bed. But it is not an easy matter to identify these two, yet in a careful comparison, also taking into consideration the nature of the coal, a separation can be made.

Unfortunately, the Lower Freeport was not sampled in Ohio. Several samples, supposedly from this bed, were taken, but on careful comparison microscopically, these samples were classed as Upper Freeport, later confirmed by geological investigations.

In Ohio the most difficult coals to correlate are the Upper Freeport and the Middle Kittanning, lying from 90 and 120 feet below the Upper Freeport.

The characteristics of the Upper Freeport of Ohio are practically the same as in Pennsylvania. The Middle Kittanning is characterized by a few types of spores, but the total number of spores varies considerably; some samples revealed relatively few, others relatively large numbers. Two kinds of spores predominate, the Middle Kittanning pitted spore and a small smooth-walled spore; only relatively few other spores in small numbers are found. In the Dover region the smooth-walled spore is predominant; in the Coshocton region the two are found in about equal numbers; and in the Hocking Valley region the pitted spore predominates. The most obvious distinction between these two beds are the large number of types of spores and the large number of nondescript spores, mostly consisting of pollens, of the Upper Freeport, contrasted with the few types of spores in the Middle Kittanning; also the larger size, the greater irregularity and larger lobing of the Upper Freeport pitted spores, as compared with the Middle Kittanning pitted spore, and the total absence of the pear-shaped spore in the smaller size and greater regularity of form of the Middle Kittanning pitted spore. The general appearance and nature of the coal substances differ in the two beds, and can also be made use of in separating them.

SUMMARY AND CONCLUSIONS.

A study of the important coal beds of the Allegheny formation in western Pennsylvania and eastern Ohio has been made to determine the microscopic characteristics of each bed which may be used for correlation purposes.

Samples were obtained from 37 representative coal mines; thin sections of the coal were prepared, and were examined microscopically.

As a result of this investigation it has been found possible to correlate each bed by means of spores and other structures found therein.

Distinct spore forms were observed in the coal of the five beds examined. These spores have been described, provisionally named, and photographed.

APPENDIX: SPORES OF THE MONONGAHELA COAL BEDS[1]

PITTSBURGH BED.

Pittsburgh spore.—(Plates II A and B) Relatively small, rather thick-walled; diameter, 15 to 16 microns; roughly circular or ovate; surface molded into closely-folded, blunt, serpentine ridges arranged symmetrically with respect to the tetrasporic mark; tetrasporic mark usually on periphery of disc and seldom across it;

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[1] Thiessen and Staud, work cited.

somewhat irregular sawtoothed or crinkled appearance in vertical section; predominant in and characteristic of the bed.

Pittsburgh megaspore.—(Plate I) Diameter about 100 microns; surface figured by a complex system of rather irregular short ridges, irregular in orientation; found in small numbers but characteristic in the bed.

Besides these two, several other spores are found—particularly a large smooth, thick-walled megaspore, about two millimeters in diameter; a smooth thick-walled microspore, and a large thin-walled spore.

REDSTONE BED.

Double-coated granular spore.—(Plate III B) Diameter variable, 55 to 2000 microns; shape irregular, often lenticular; usually more or less folded upon itself; wall composed of two layers—an outer, light-yellow, very granular one and an inner, brownish-yellow, thinner and less granular one; found fairly uniformly distributed from top to bottom of Redstone bed and in lesser numbers in the Sewickley bed.

Redstone-Sewickley megaspore.—Plate III A) Diameter, 70 to 90 microns; shape, regular; thick-walled; in considerable numbers in top coal but rarely in bottom; fairly predominant in Sewickley bed.

Redstone megaspore.—(Plates II C and D) Diameter, somewhat greater than Redstone-Sewickley megaspore; surface covered with short echinate spines whose bases form rough hexagons; rare.

SEWICKLEY BED.

Sewickley spore.—(Plates III C and D) Diameter, 18 to 20 by 20 to 25 microns, the disc usually oval; surface configuration consists of broad and blunt echinate spines or humps; found in this bed only.

Redstone-Sewickley megaspore.—(Plate III A) As found in the Sewickley bed; diameter, 60 to 70 microns; thickness, 5 to 10 microns; surface, smooth or with a few elevations.

Double-coated granular spore.—(Plate III B)) Described already as one of Redstone spores.

The Redstone megaspore type is also, but rarely, found in the Sewickley bed.

MAPS
and
PLATES.

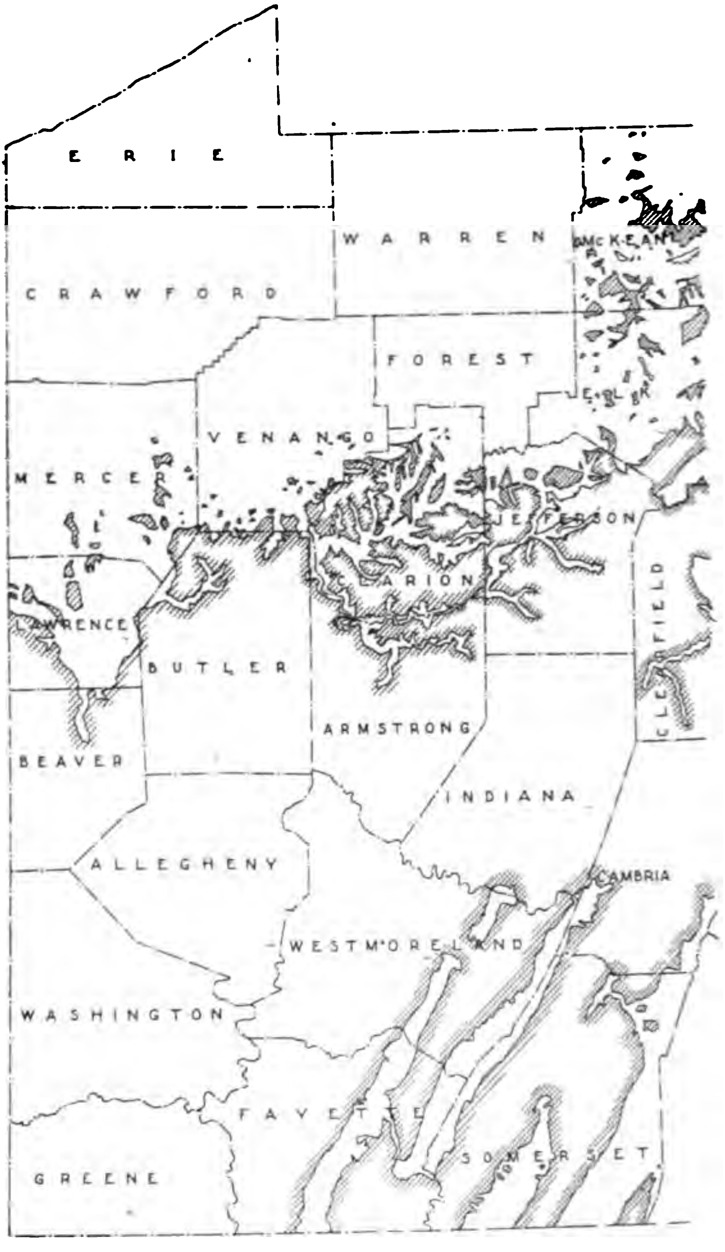

FIGURE 1.—*Map showing outcrop of and area underlain by Lower Kittanning bed in Western Pennsylvania (Pennsylvania Geologic and Topographic Survey).*

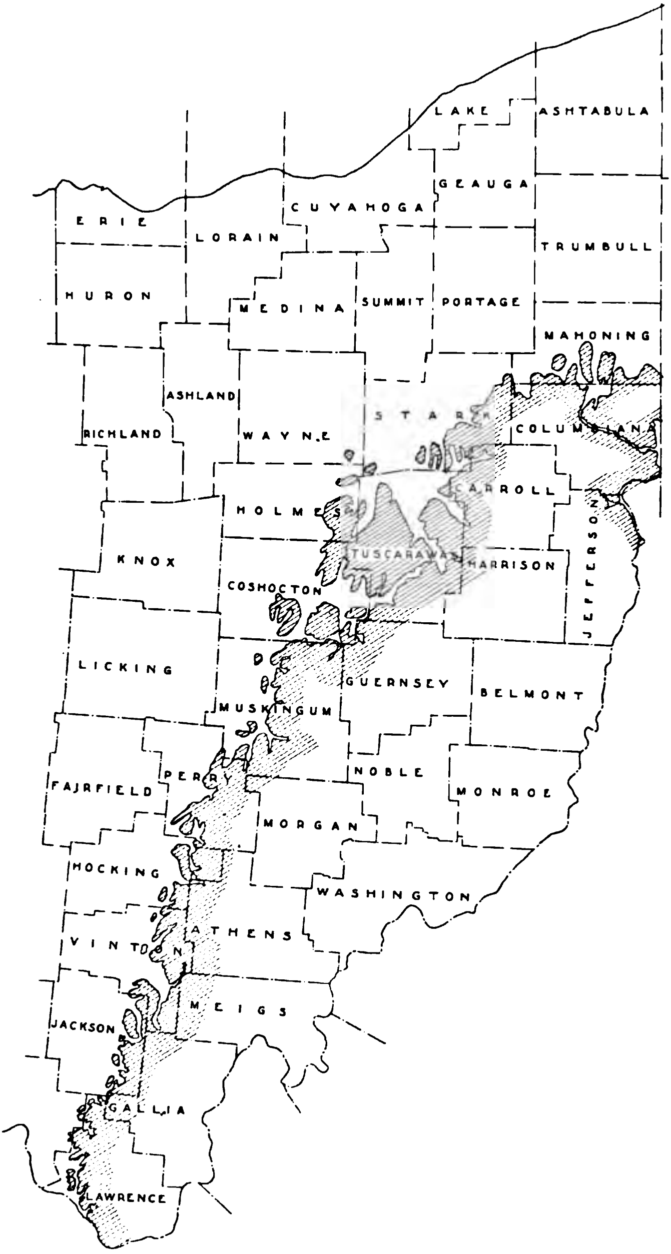

FIGURE 11.—*Map showing outcrop of and area underlain by Middle Kittanning bed in Eastern Ohio (Geological Survey of Ohio).*

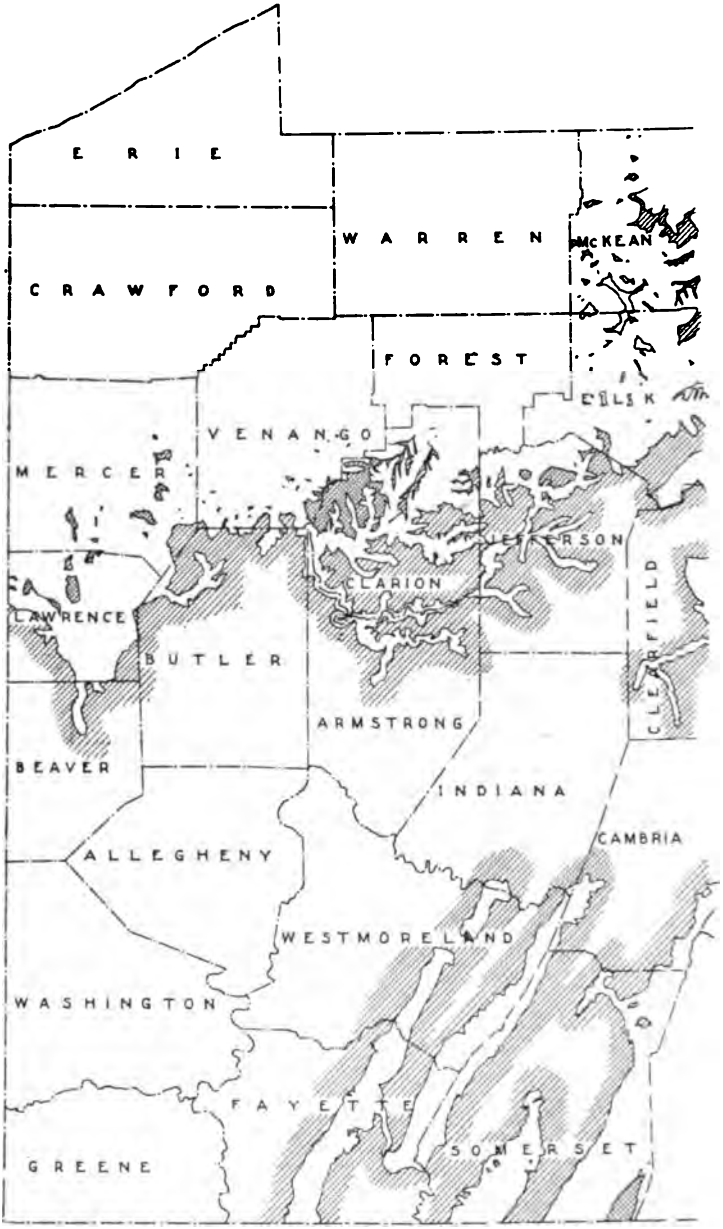

FIGURE III.—*Map showing outcrop of and area underlain by Upper Kittanning bed in Western Pennsylvania (Pennsylvania Geologic and Topographic Survey).*

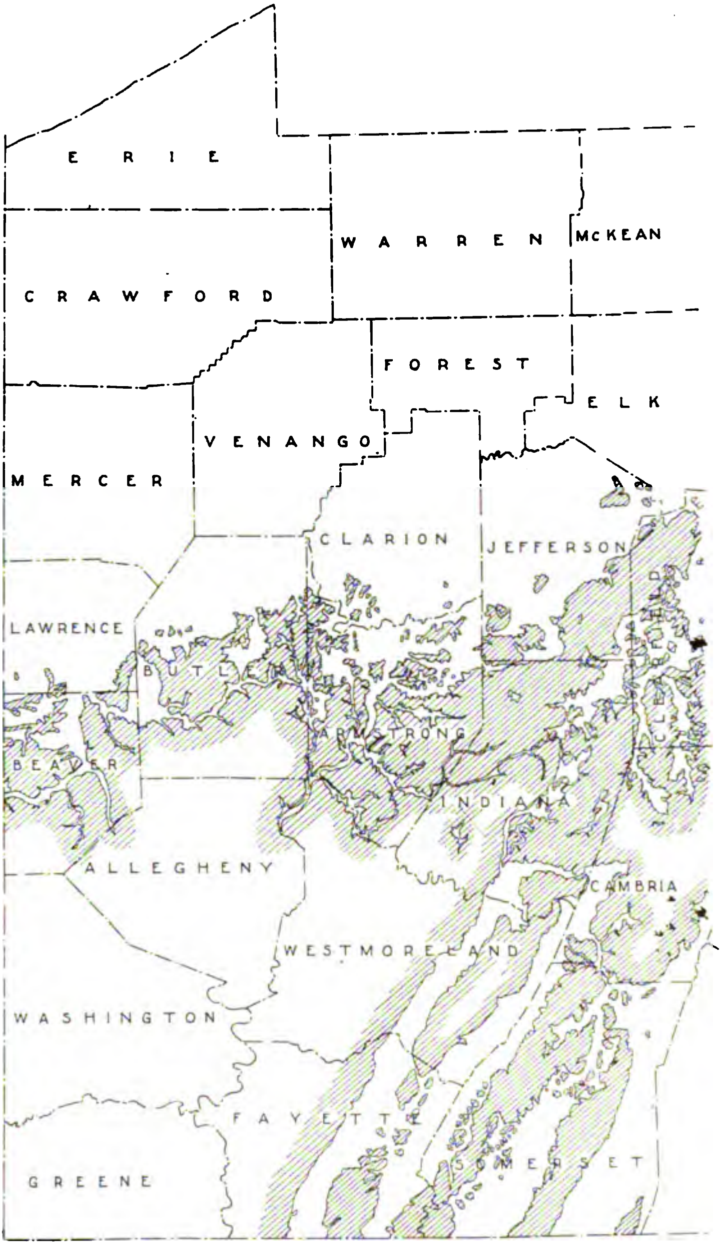

Figure IV.—*Map showing outcrop of and area underlain by Lower Freeport bed in Western Pennsylvania (Pennsylvania Geologic and Topographic Survey).*

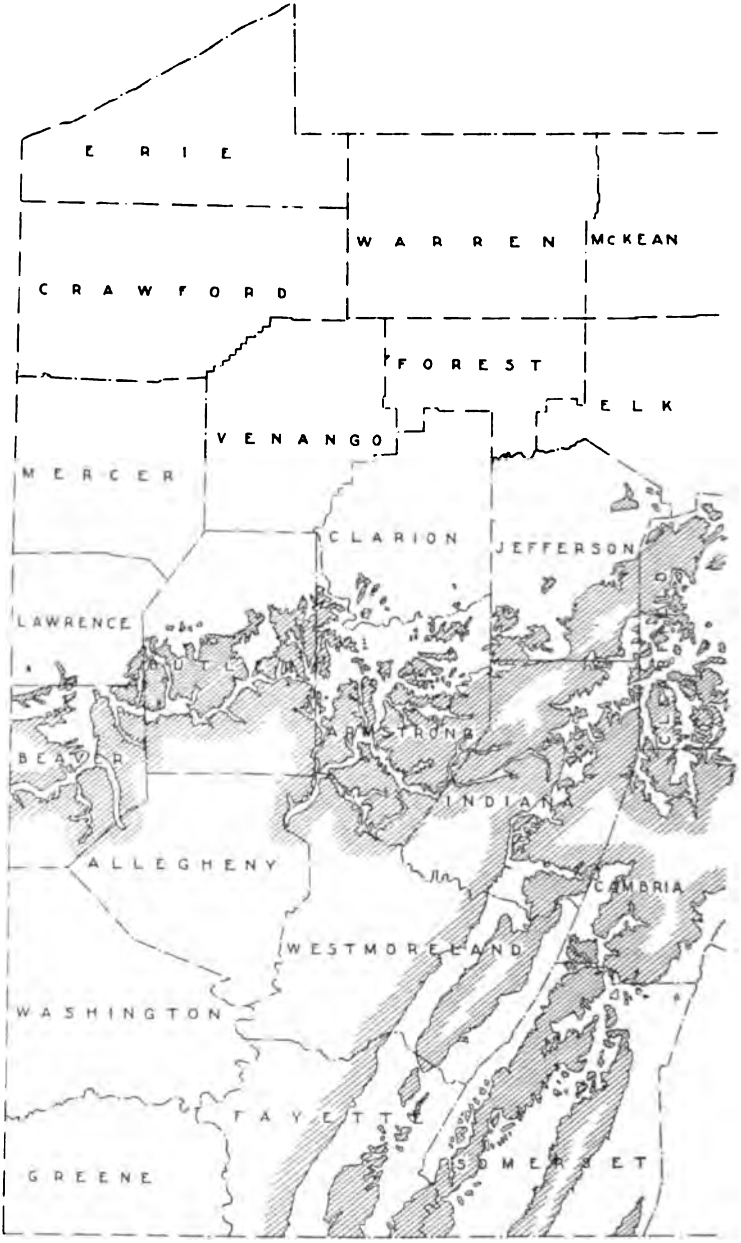

FIGURE V.—*Map showing outcrop of and area underlain by Upper Freeport bed in Western Pennsylvania (Pennsylvania Geologic and Topographic Survey).*

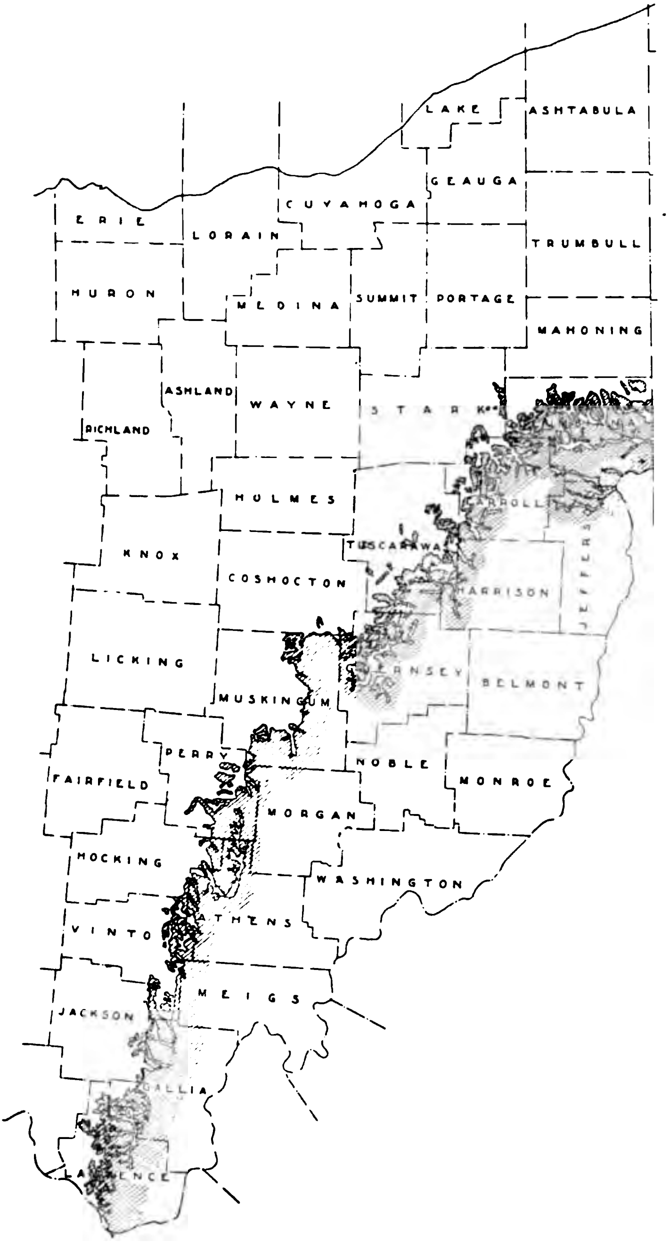

FIGURE VI.—*Map showing outcrop of and area underlain by Upper Freeport bed in Eastern Ohio (Geological Survey of Ohio).*

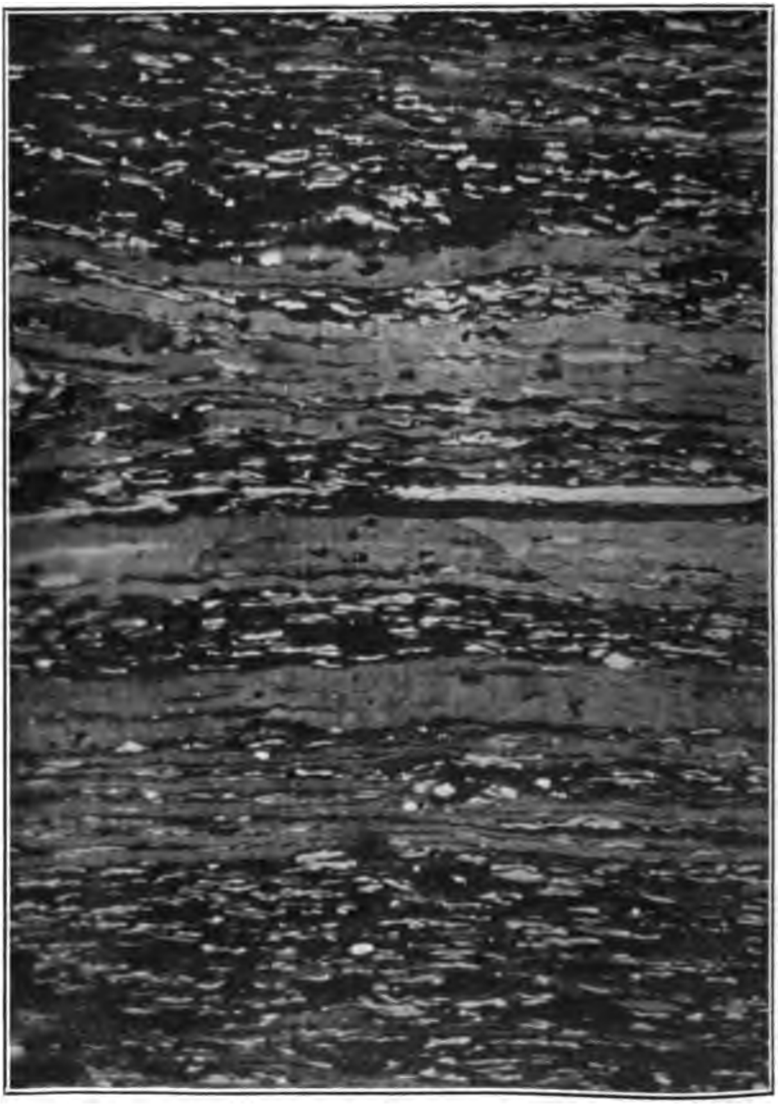

PLATE I.—*Cross thin section of coal from Lower Kittanning bed at Furnace Run, near Kittanning, Armstrong County, Pa., showing Lower Kittanning biconcave spore. X 200.*

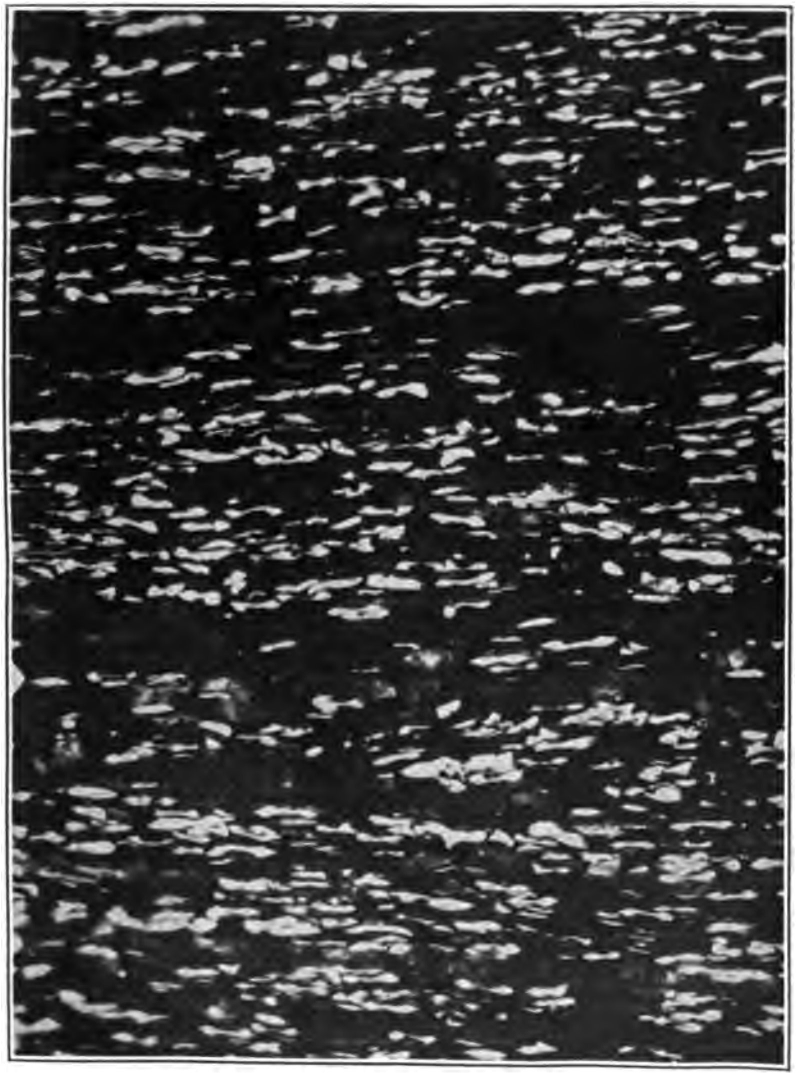

Plate II.—*Cross thin section of coal from Lower Kittanning bed at Leesburg, Mercer County, Pa., showing the Lower Freeport biconcave spore. X 200*

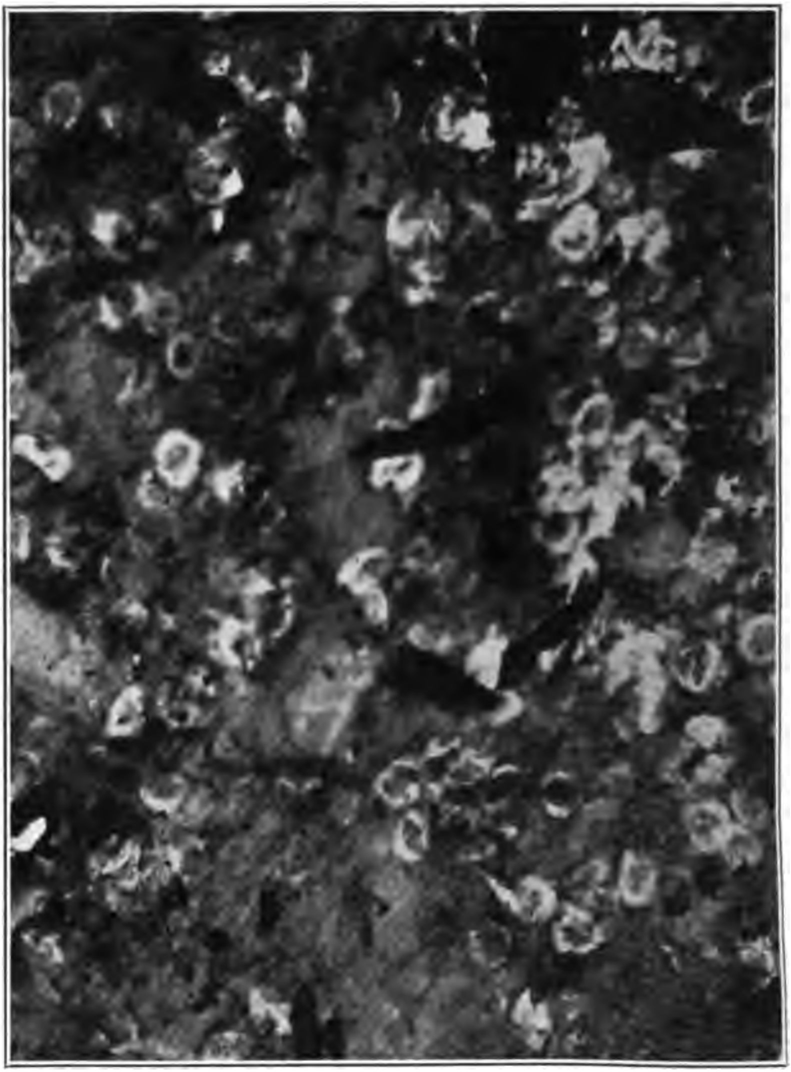

Plate III.—*Horizontal thin section of coal from Lower Kittanning bed at Cadogan, Armstrong County, Pa., showing the Lower Kittanning biconcave spore. X200.*

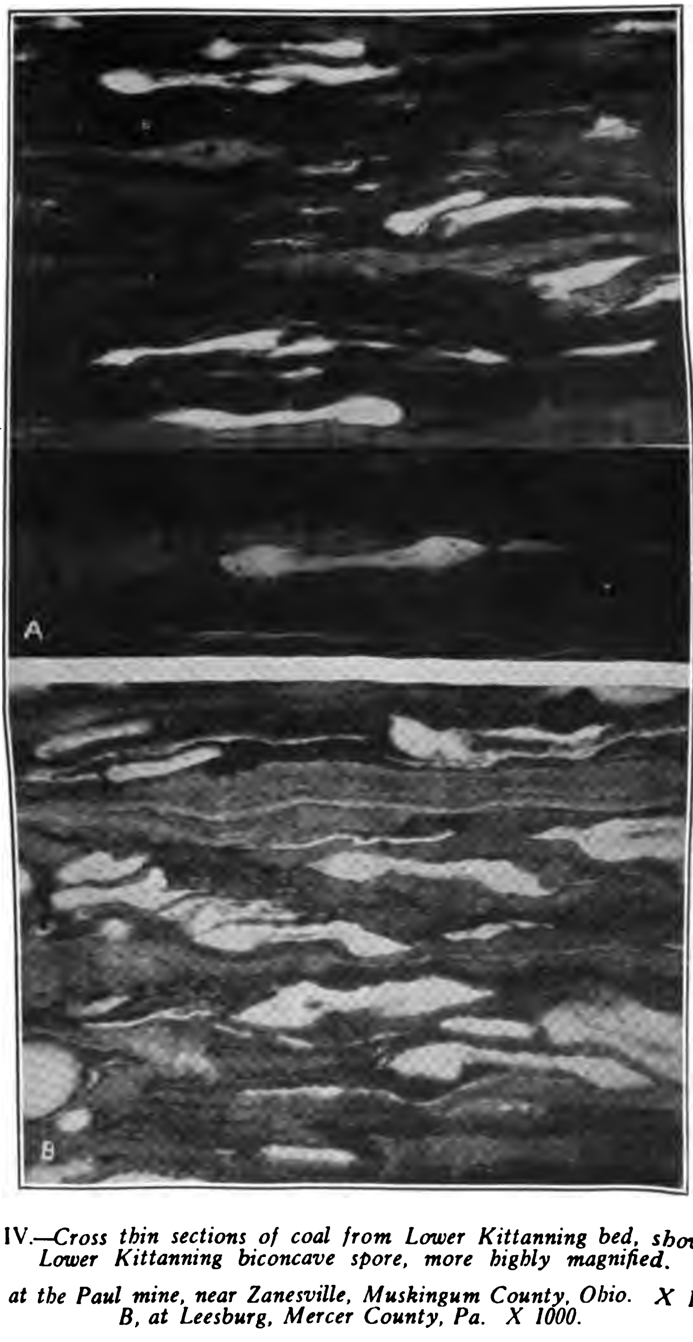

Plate IV.—*Cross thin sections of coal from Lower Kittanning bed, showing the Lower Kittanning biconcave spore, more highly magnified.*

A, at the Paul mine, near Zanesville, Muskingum County, Ohio. X 1000. B, at Leesburg, Mercer County, Pa. X 1000.

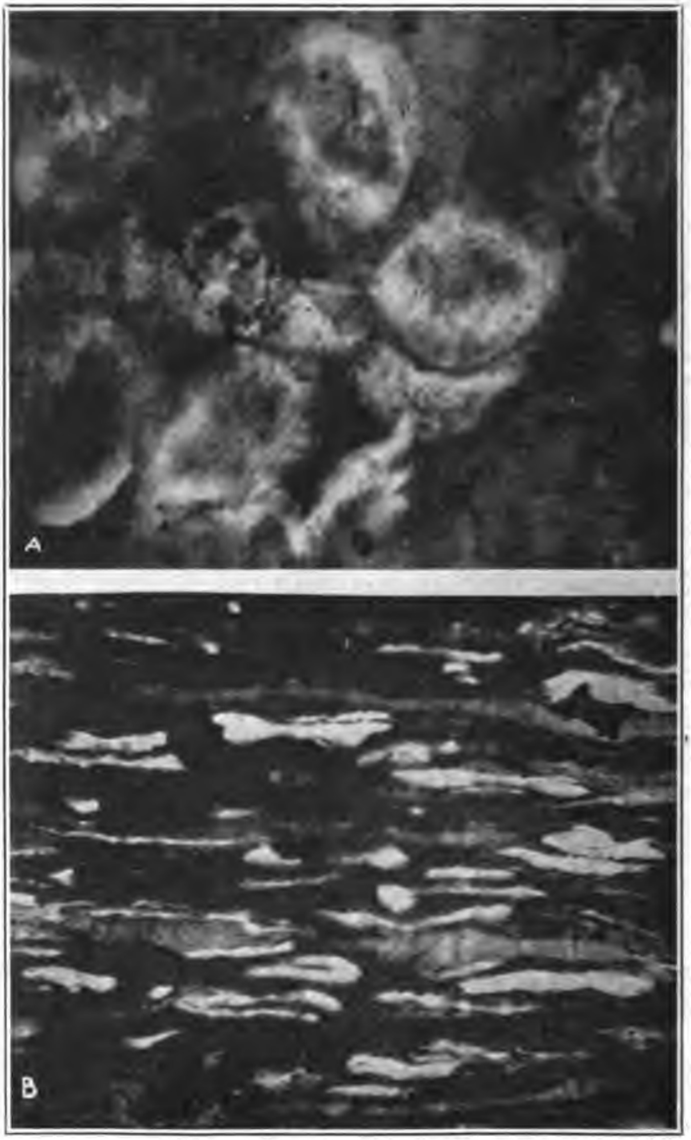

Plate V.—*Thin sections of coal from Lower Kittanning bed at Cadogan Mine No. 1, Cadogan, Armstrong County, Pa., showing the biconcave spore highly magnified.*

A, Horizontal section. X 1000.
B, Cross section. X 1000.

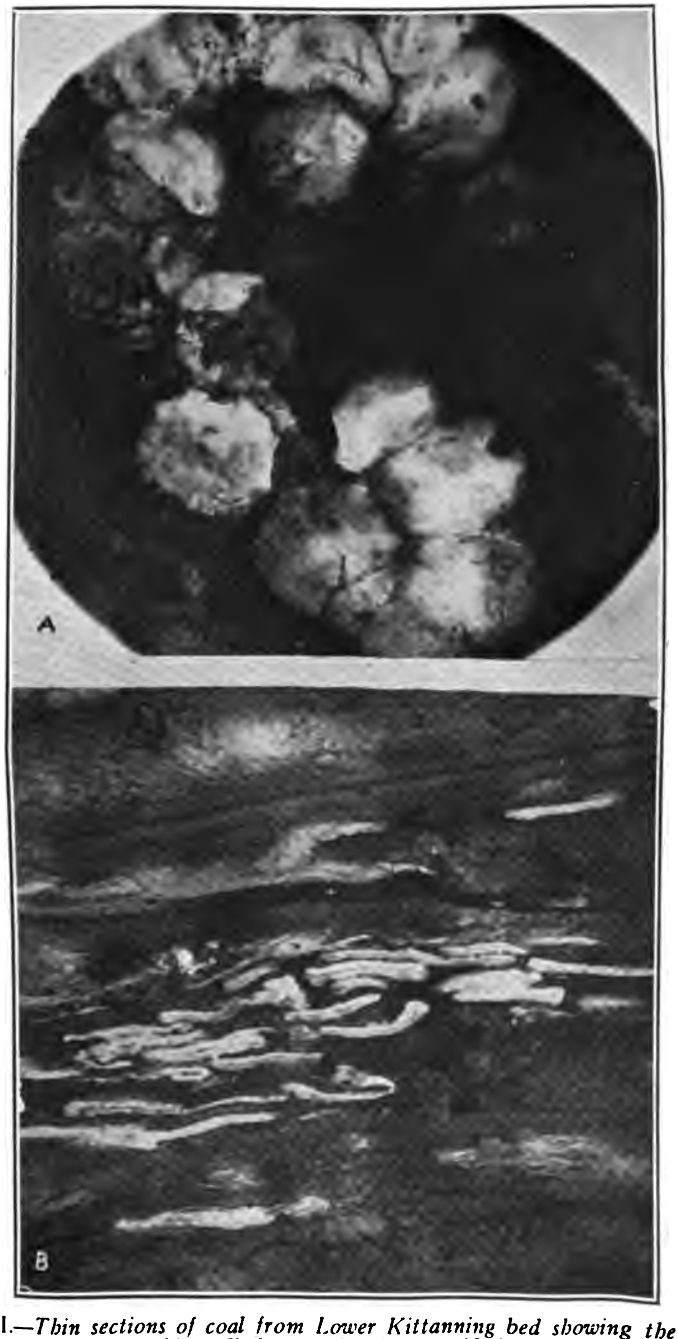

PLATE VI.—*Thin sections of coal from Lower Kittanning bed showing the smooth thin-walled spore, highly magnified.*

A, Horizontal section. X1000.
B, Cross section. X 1000.

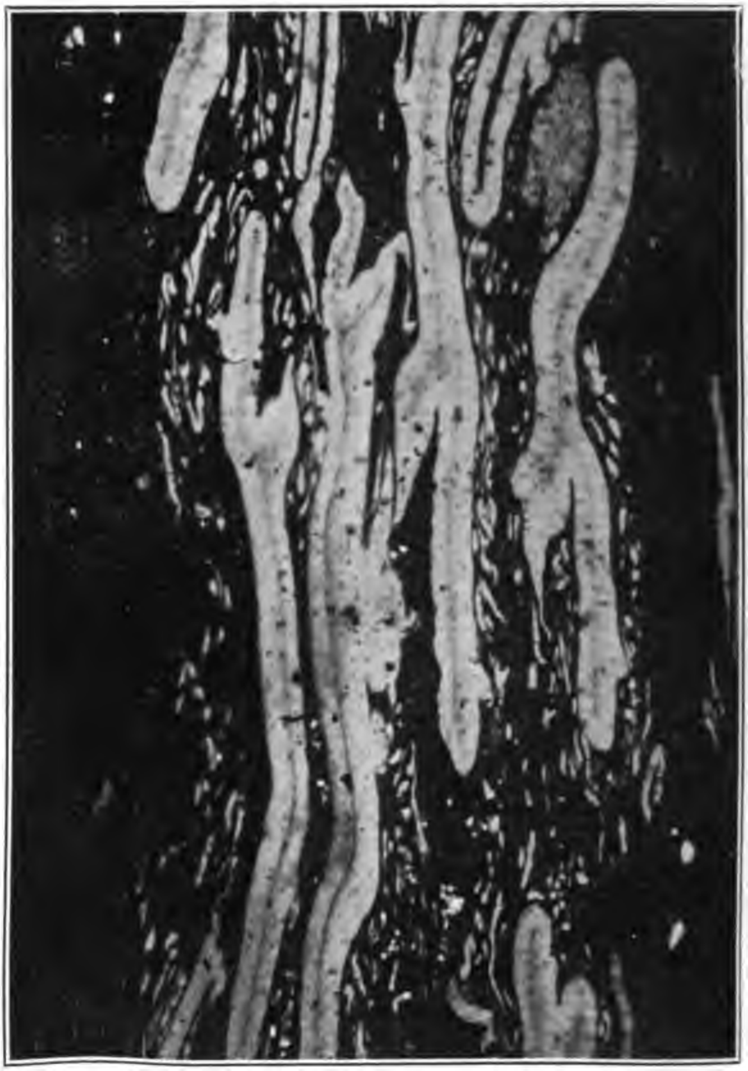

Plate VII.—*Cross thin section of coal from Lower Kittanning bed at Cadogan Mine No. 1, Cadogan, Armstrong County, Pa., showing megaspores and miscrospores and their relative sizes. X 200.*

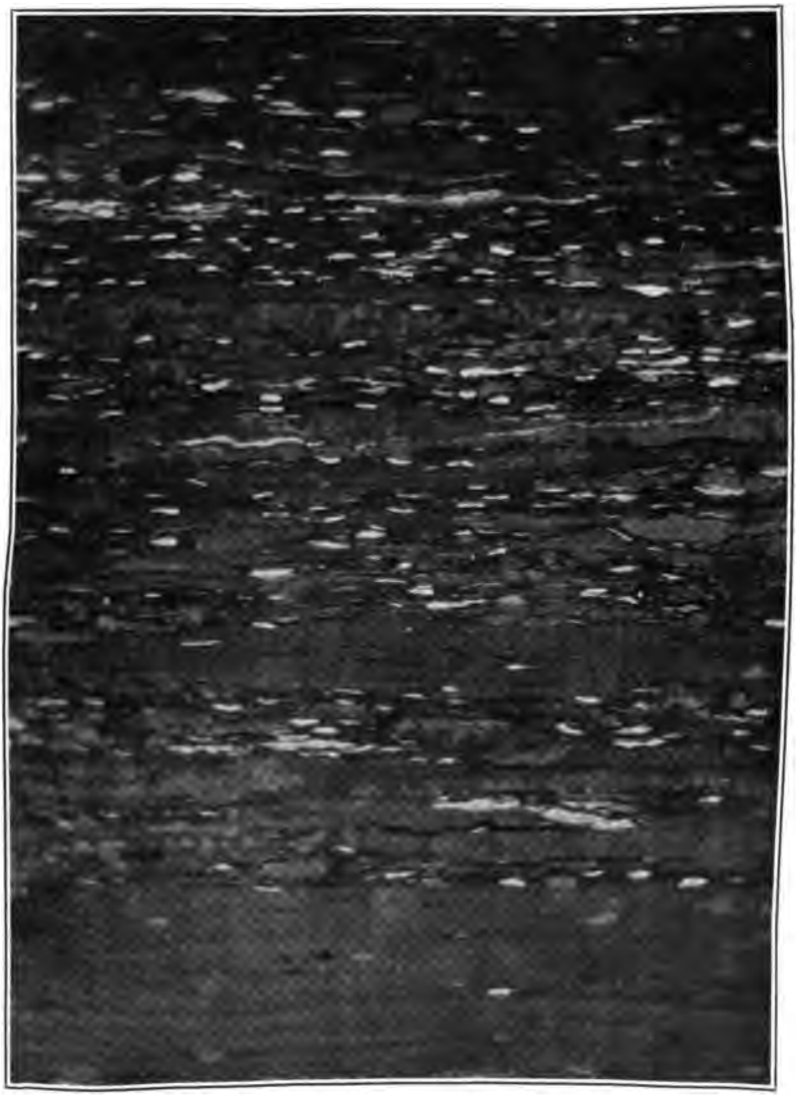

Plate VIII.—*Cross thin section of coal from Middle Kittanning bed at Paul mine, Zanesville, Muskingum County, Ohio, showing general appearance of dull coal, with the Middle Kittanning pitted microspore. X 200.*

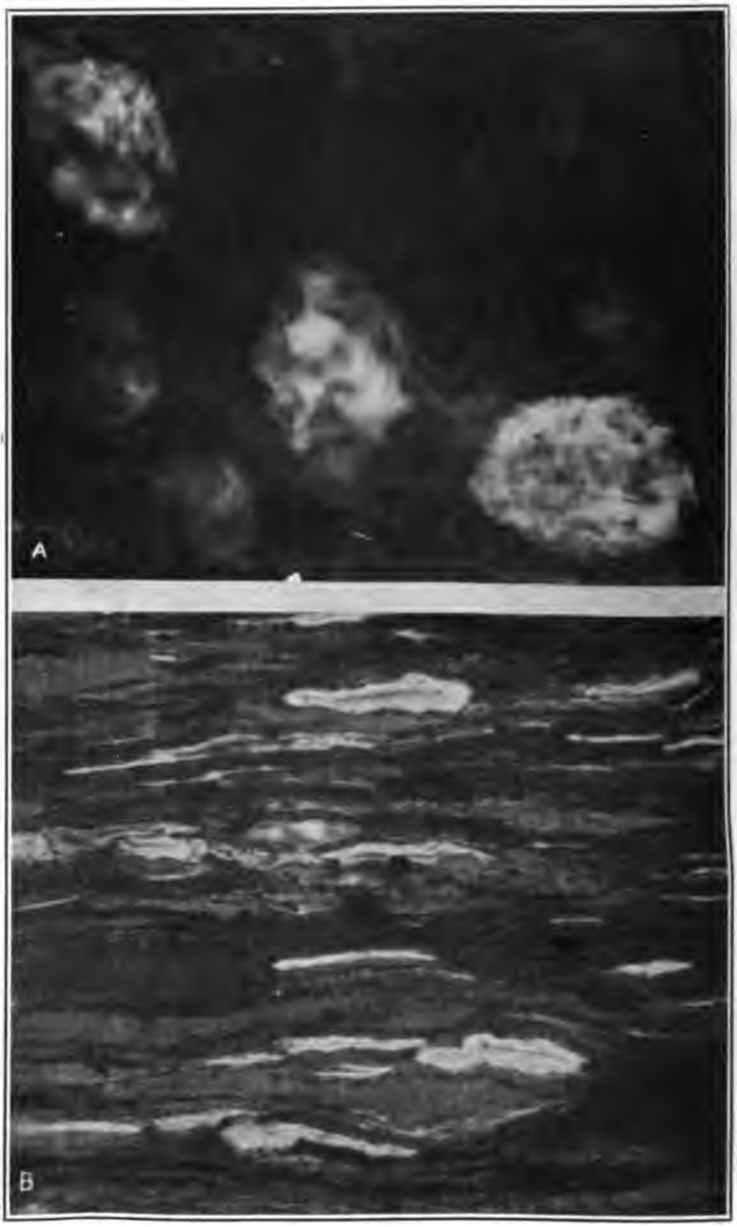

Plate IX.—*Thin sections of coal from Middle Kittanning bed at Paul Mine, Zanesville, Muskingum County, Ohio; showing the Middle Kittanning pitted spore, more highly magnified.*

A, Horizontal section. X 1000.
B, Cross section. X 1000.

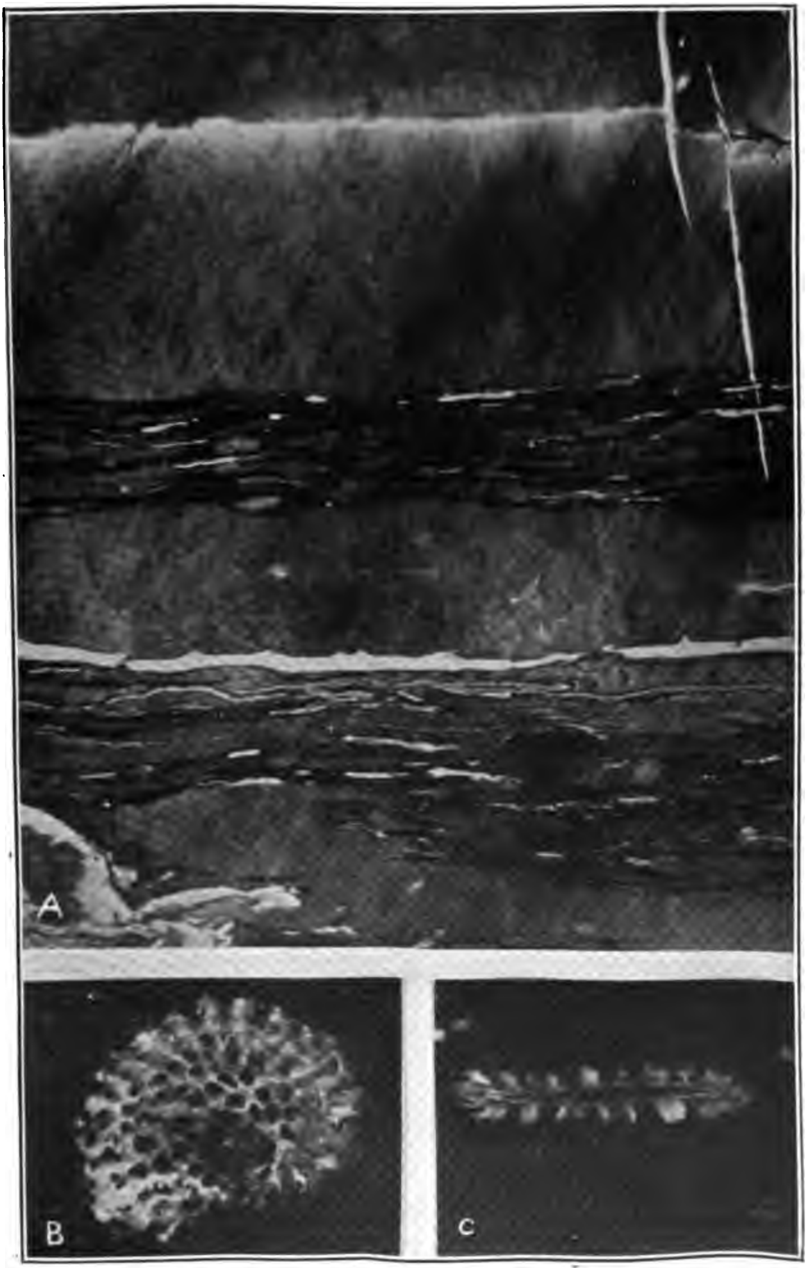

Plate X.—*A, Cross thin section of Upper Kittanning bed at New Bethlehem, Pa., containing the finely pitted spore and the large zoned spore in the attritus. X 200.*

B and C, Deeply pitted microspore. X 1000.

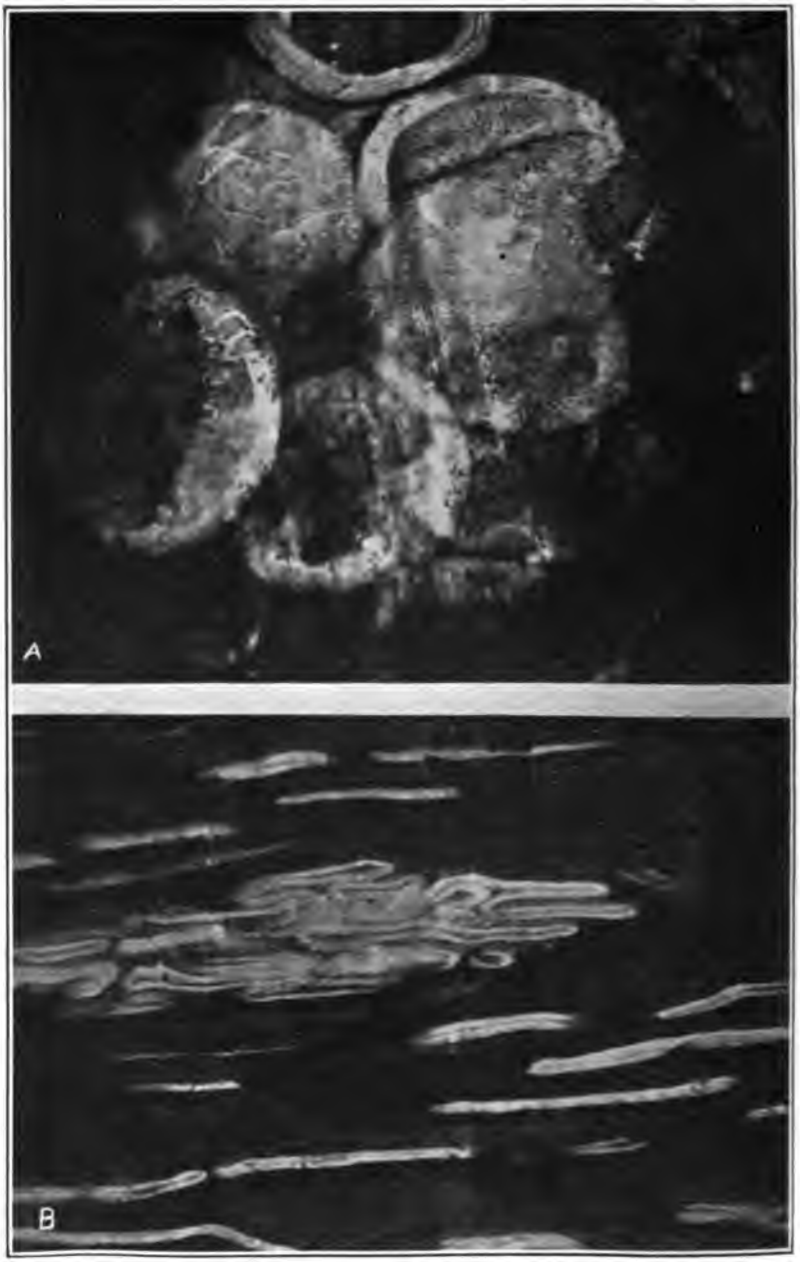

PLATE XI.—*Thin cross sections of coal from Upper Kittanning bed, at New Bethlehem, Pa., showing the Upper Kittanning finely pitted spore at a high magnification.*
A, Horizontal section. X 1000.
B, Cross section. X 1000.

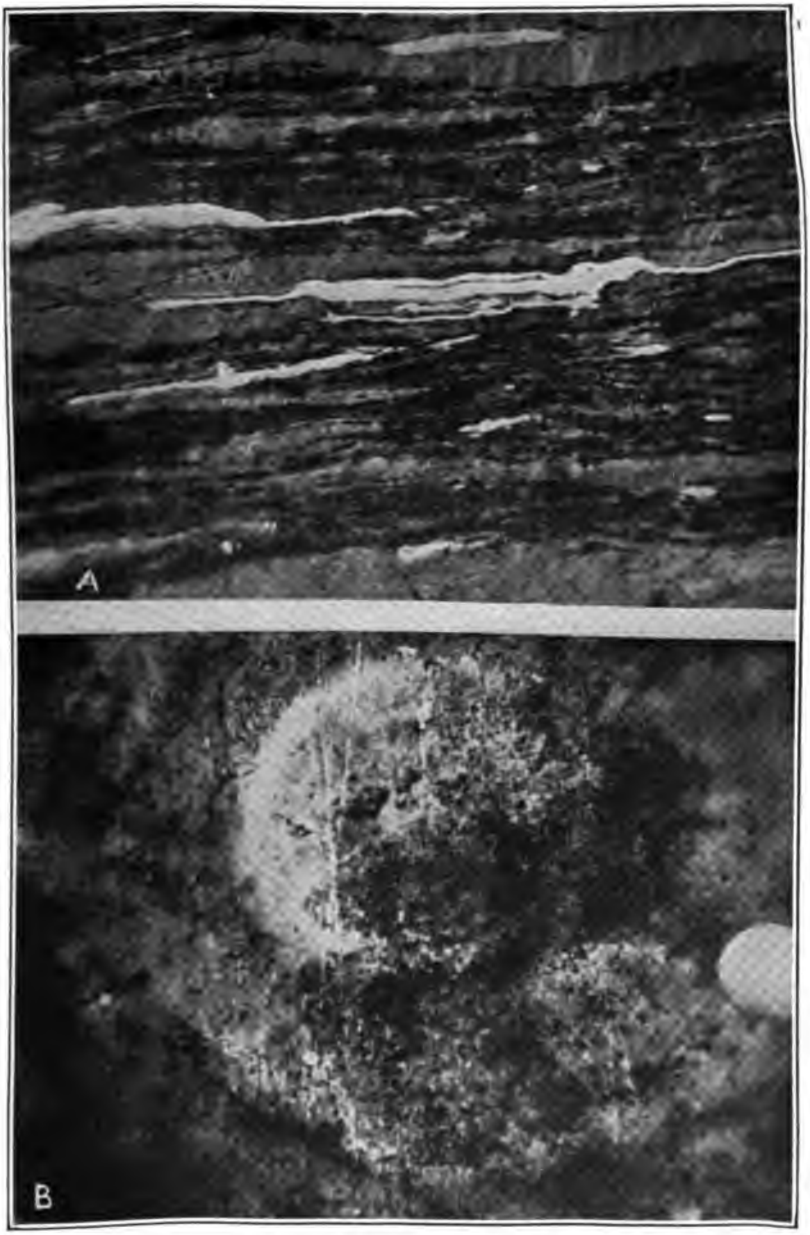

Plate XII.—*Thin sections of coal from Upper Kittanning bed at New Bethlehem, Pa., at a low magnification showing the zoned microspore.*

A, Cross section. X 1000.
B, Horizontal section. X 1000.

PLATE XIII.—*Cross thin section of coal from Lower Freeport bed at Cadogan Mine No. 4, Cadogan, Armstrong County, Pa., showing attritus with a number of different spores. X 200.*

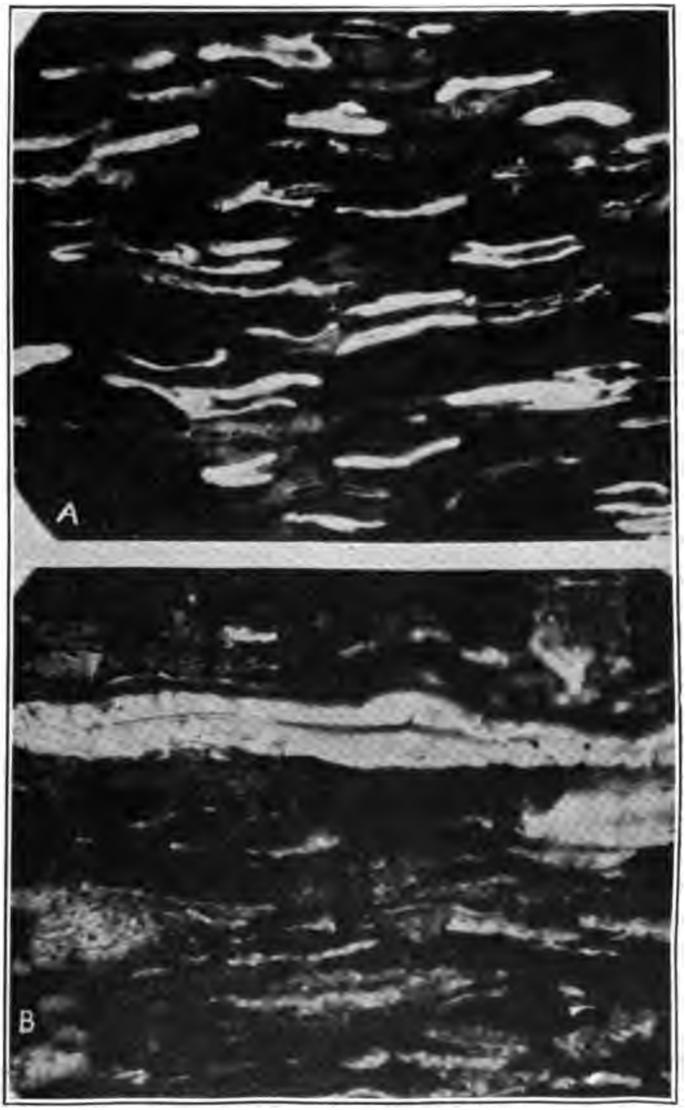

Plate XIV.—*Cross thin sections of coal from Lower Freeport bed at Cadogan Mine No. 4, Cadogan, Armstrong County, Pa.*

A, Section showing small thick walled microspores. X 1000.
B, Section containing the same spore, poorly preserved and a large microspore occasionally found. X 1000.

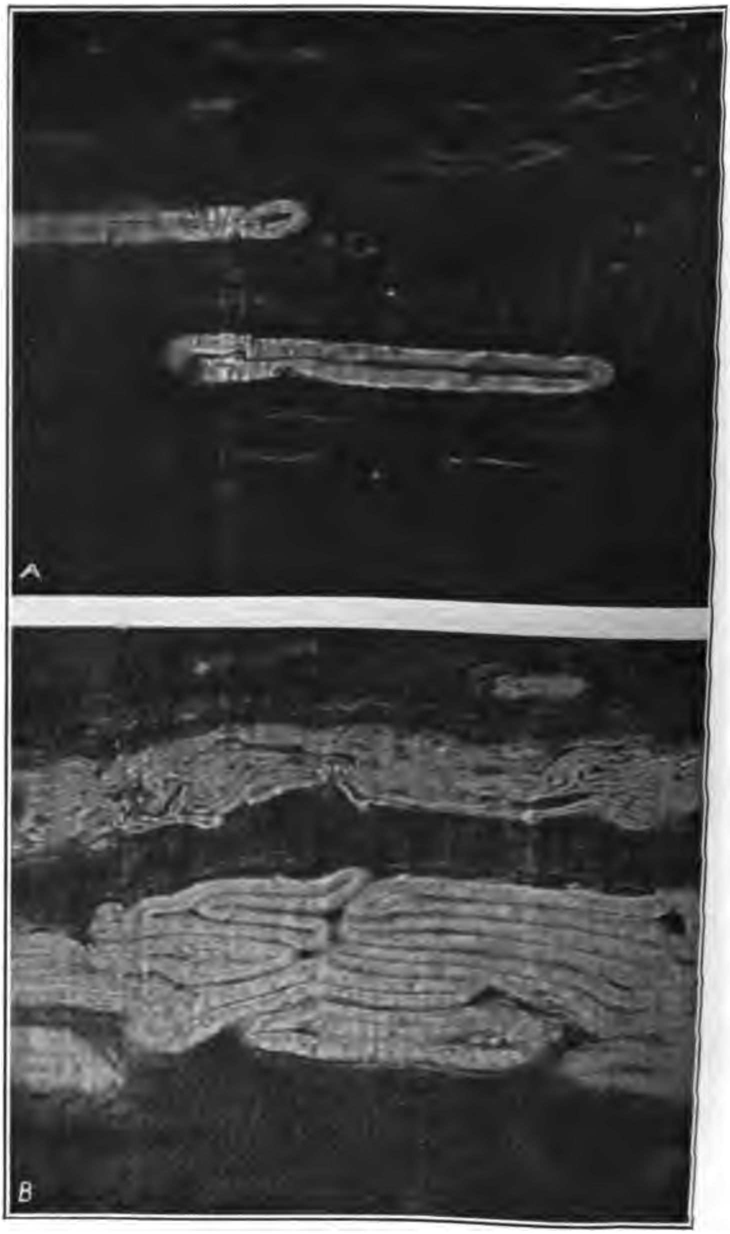

Plate XV.—*Cross thin sections of coal from Lower Freeport bed, showing finely pitted microspore.*

A, Single spores. X 1000.
B, Spores in a mat. X 1000.

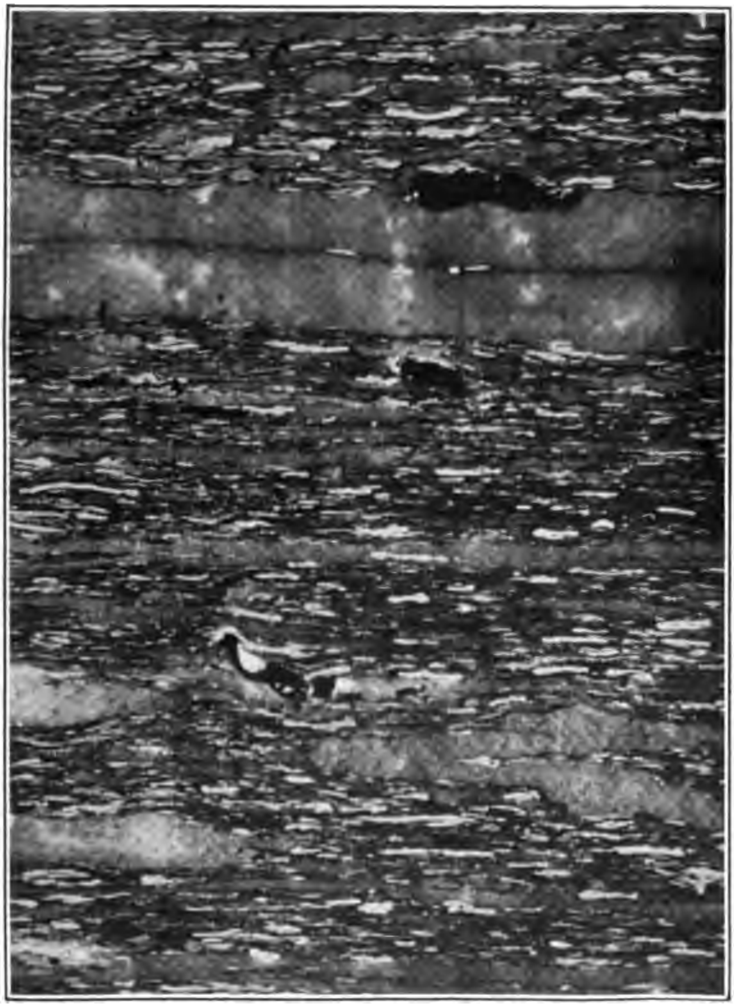

Plate XVI.—*Cross thin section of coal from Upper Freeport bed at Kerr mine near Freeport, Pa., showing an attritus with a large number of spores. X 200.*

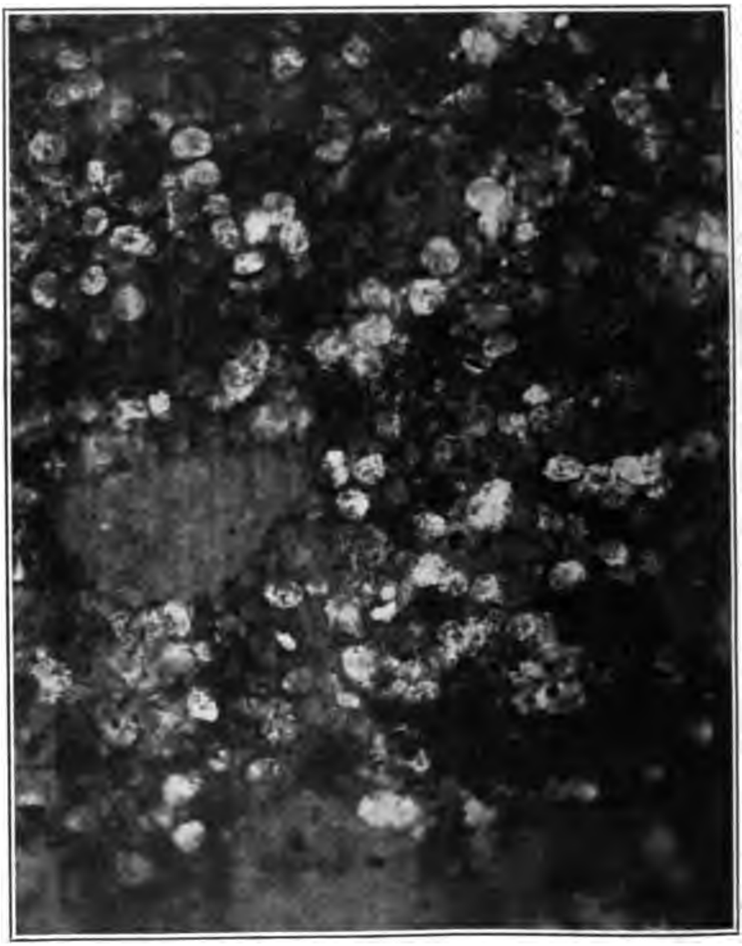

Plate XVII.—*Horizontal thin section of coal from Upper Freeport bed at Maple Leaf Mine, near Uhrichsville, Ohio, showing a large number of spores in which the characteristic pitted microspore predominates. X 200.*

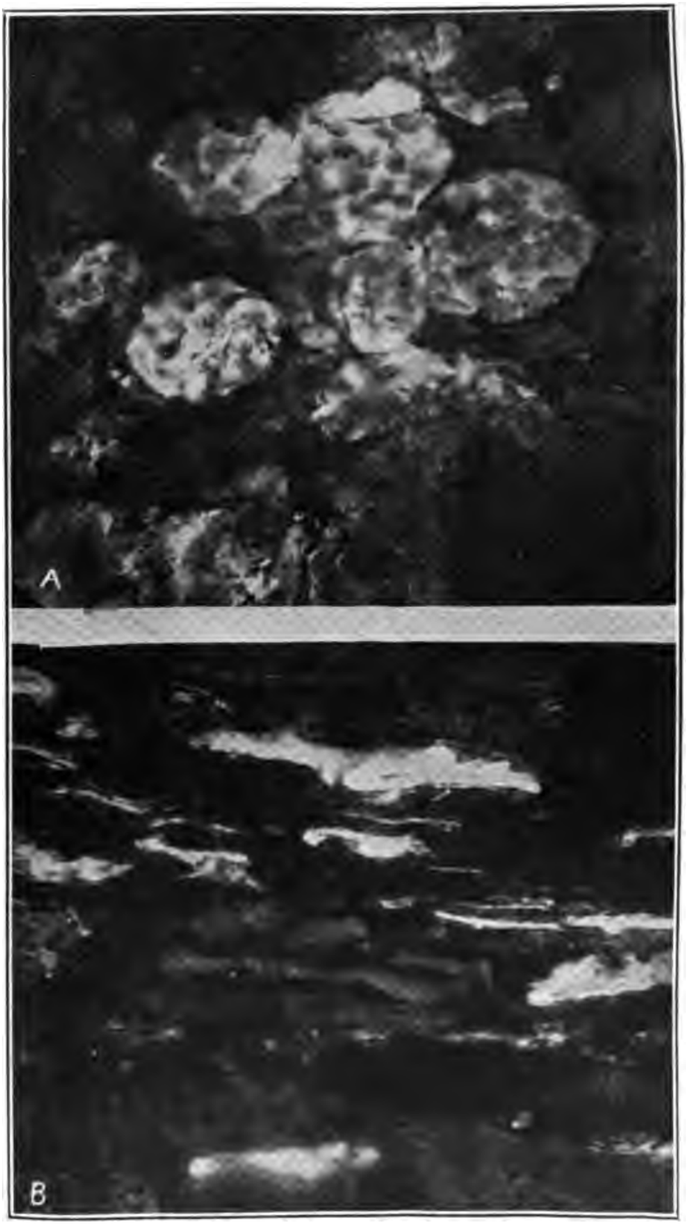

Plate XVIII.—*Thin section of coal from Upper Freeport bed at a high magnification.*

A, Horizontal section showing detail of the Upper Freeport pitted spore. X 200. B, Cross section of the same. X 1000.

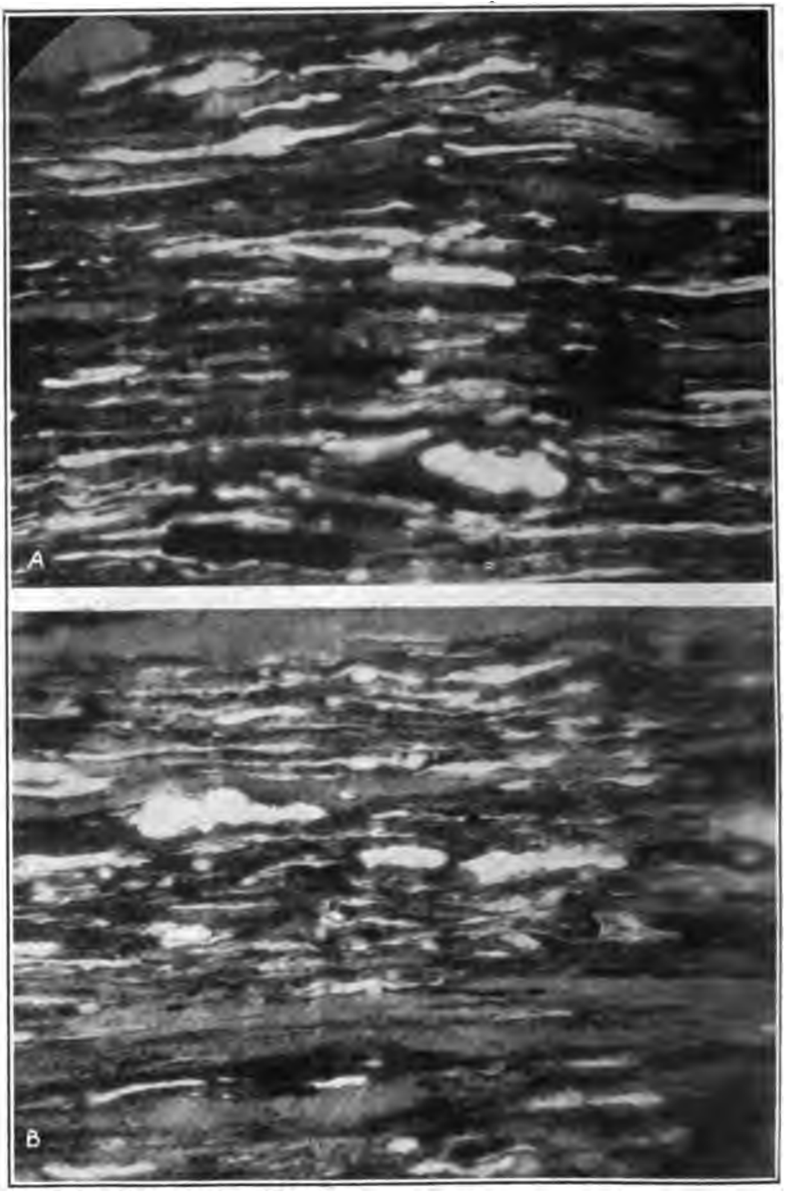

Plate XIX.—*Cross thin sections of coal from Upper Freeport bed, at a high magnification, showing the large number and different kinds of spores. X 1000.*

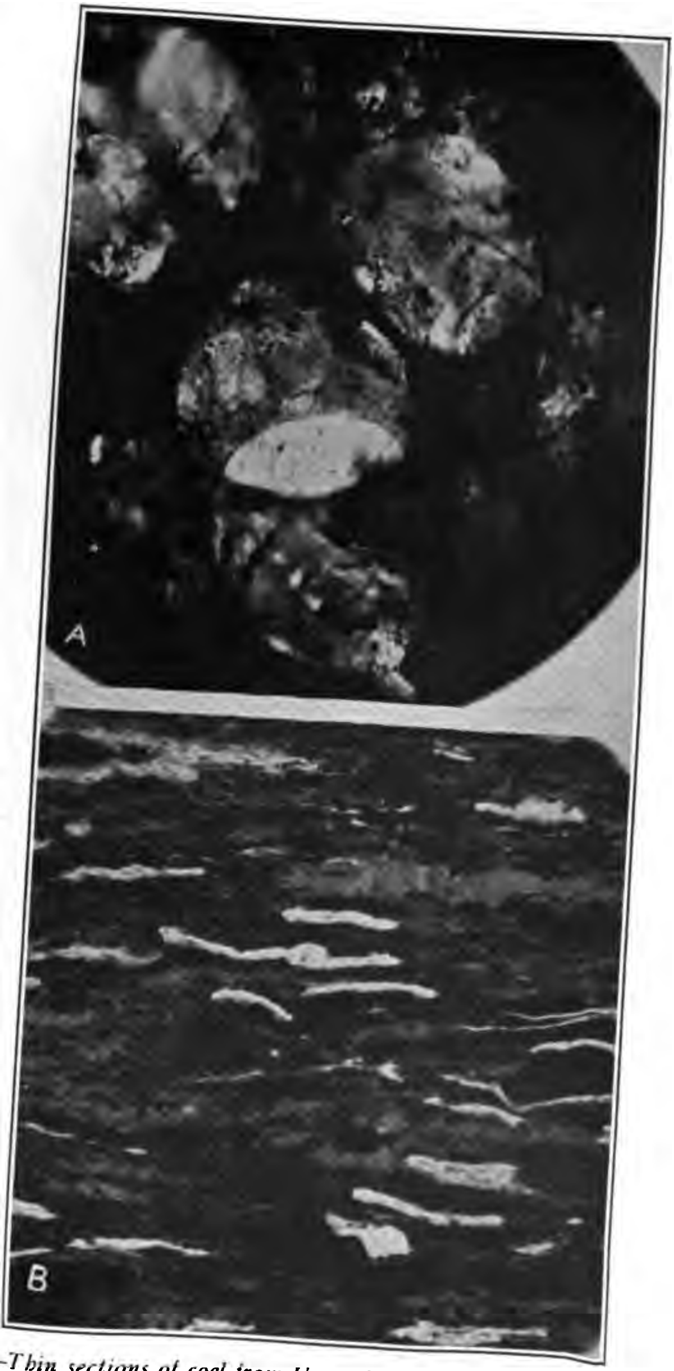

PLATE XX.—*Thin sections of coal from Upper Freeport bed at high magnification, showing the small smooth microspore.*
A, Horizontal section. X 1000.
B, Cross section. X 1000.

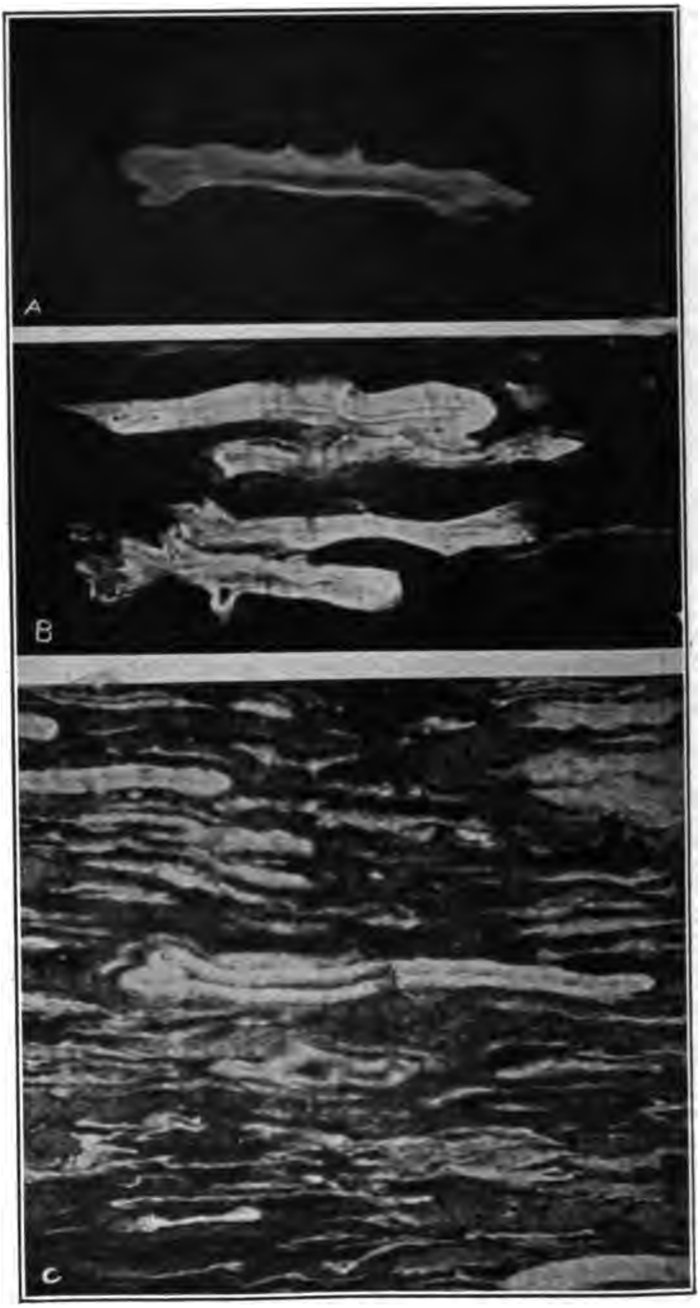

Plate XXI.—*Thin sections of coal from Upper Freeport bed, showing the Upper Freeport ridged spore.*

A and B, Cross section from Vogley mine, Butler, Pa.

C, Thin section of coal from Kerr mine, containing a large number of pollen grains and the ridged spore. X 1000.

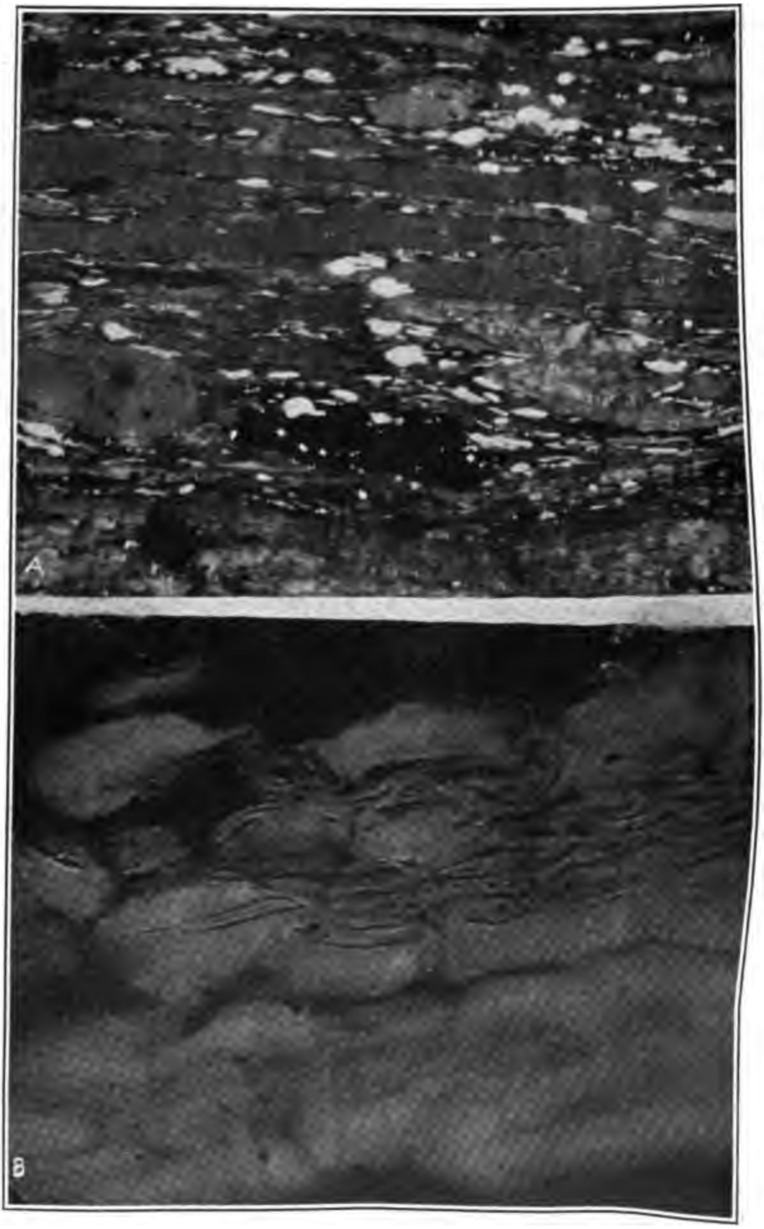

Plate XXII.—*Cross thin sections of coal from Upper Freeport bed, showing the Upper Freeport pear-shaped spore.*

A, Section of lower magnification showing several spores distributed in the coal. X 200.

B, Section at higher magnification showing the spore in a mass. X 1000.

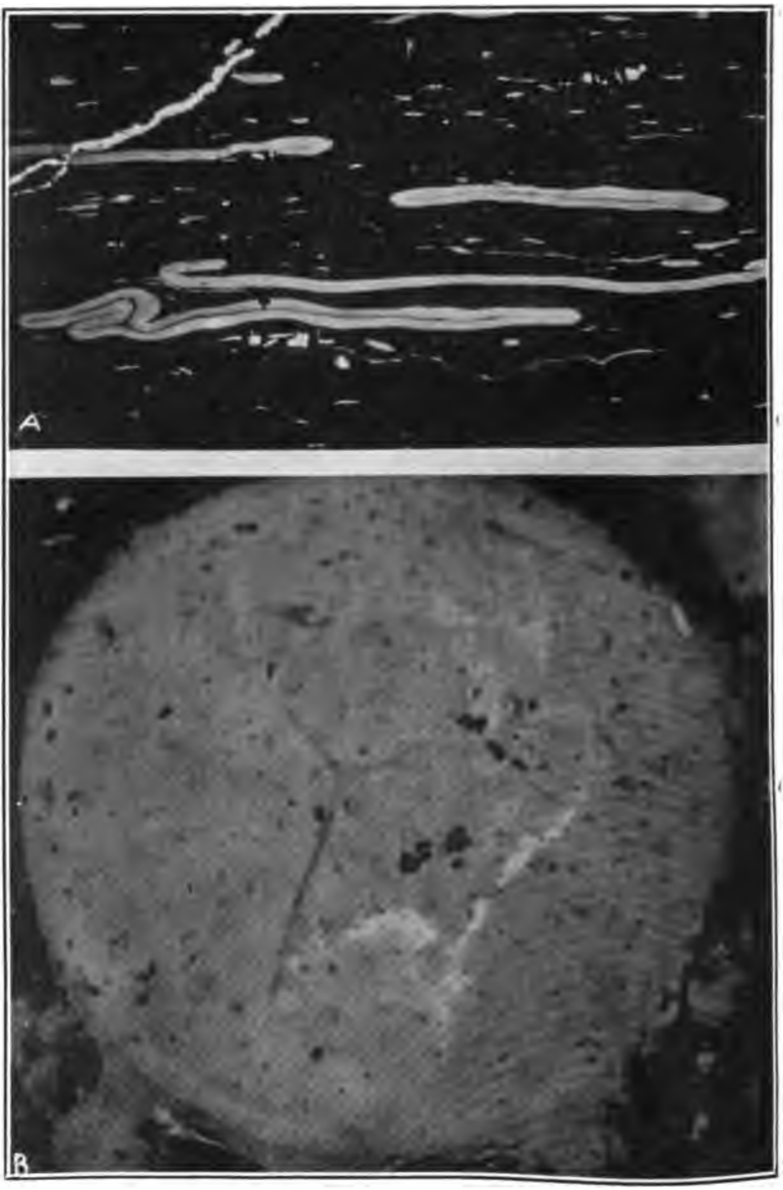

Plate XXIII.—*Thin sections of Upper Freeport coal from the Vogley mine, showing a smooth-walled megaspore.*

A, Cross section at a low magnification with several spores. X 50.
B, Horizontal section of single spore showing tetrasporic mark. X 200.

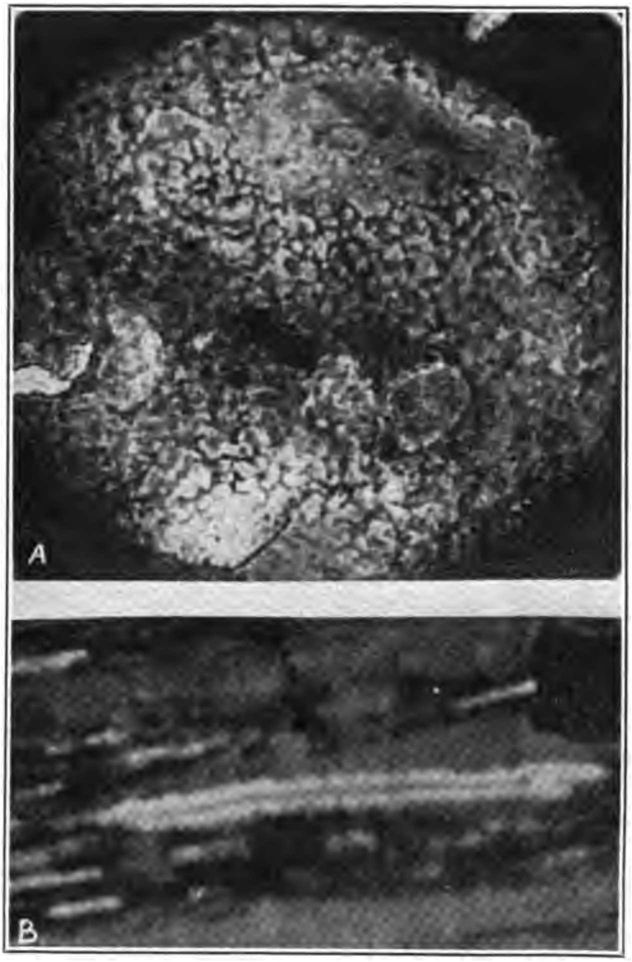

PLATE I.—*(Appendix) A, Pittsburgh megaspore, horizontal section. X 1000. B, Pittsburgh megaspore, vertical section. X 1000.*

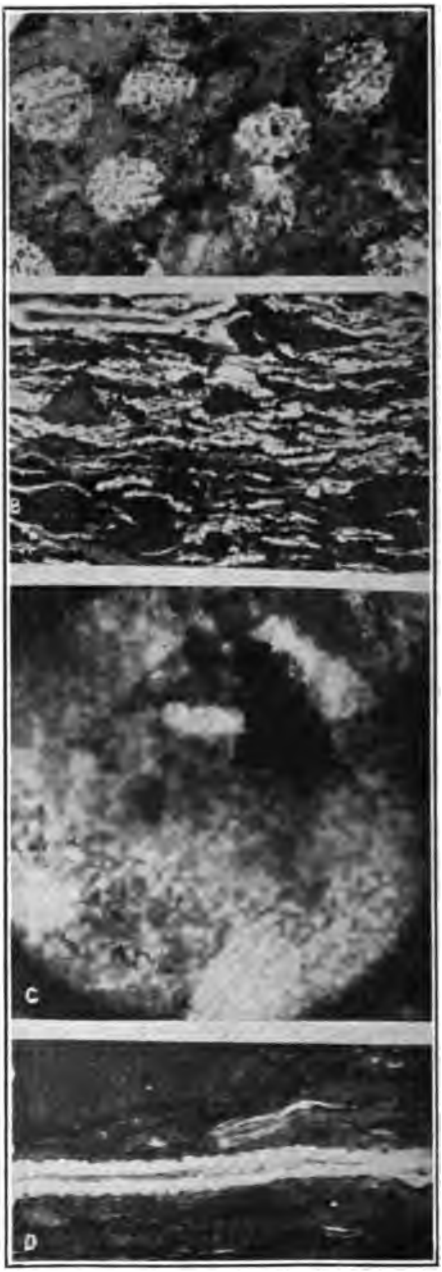

Plate II.—*(Appendix) A, Pittsburgh microspore, horizontal. X 1000.*
B, Pittsburgh microspore, vertical. X 1000.
C, Redstone megaspore, horizontal. X 1000.
D, Redstone megaspore, vertical. X 1000.

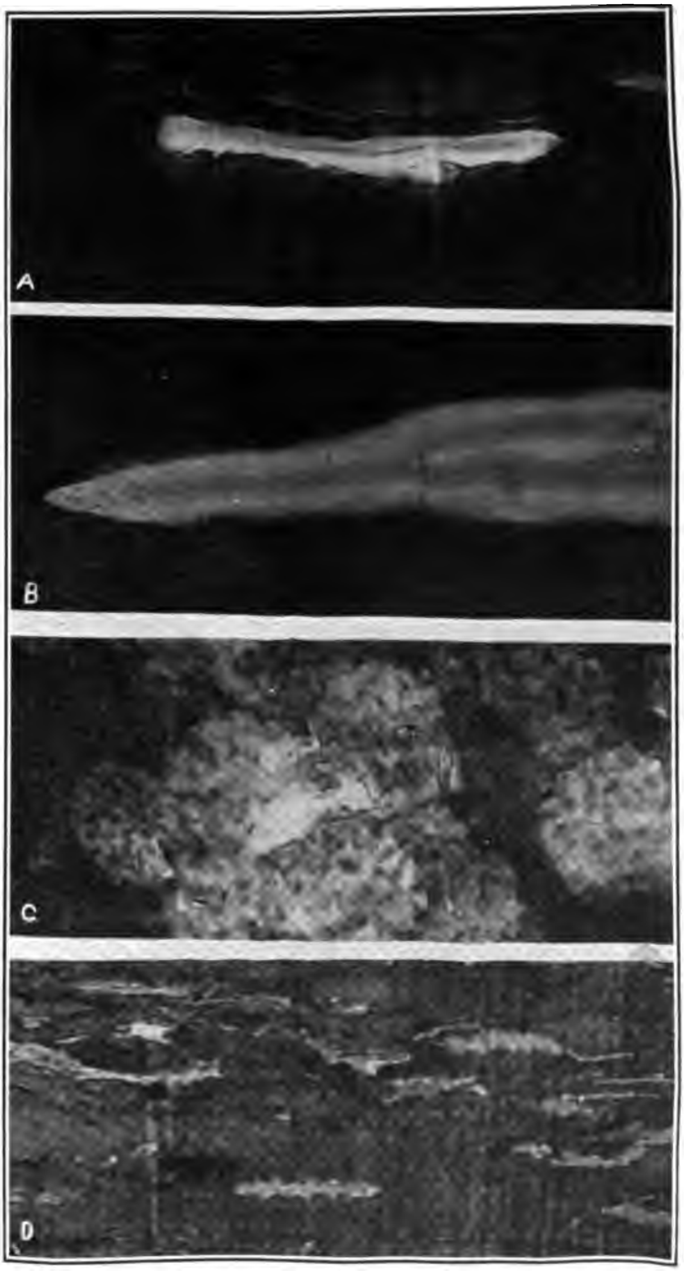

PLATE III.—*(Appendix) A, Redstone-Sewickley megaspore, vertical. X 1000.*
B, Double-coated granular spore found in both Redstone and Sewickley beds, vertical. X 1000.
C, Sewickley spore, horizontal, X 1000.
D, Sewickley spore, vertical. X 1000.

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U. S. BUREAU OF MINES, AND
ADVISORY BOARD OF COAL-MINE OPERATORS AND ENGINEERS.

CORRELATION OF COAL BEDS OF THE ALLEGHENY FORMATION OF WESTERN PENNSYLVANIA AND EASTERN OHIO.

By

REINHARDT THIESSEN, Research Chemist,
Bureau of Mines;

and

FORD E. WILSON, Research Fellow,
Carnegie Institute of Technology.

Price, 40 cents.

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